Relations Among Rainstorm Runoff, Streamflow, pH, and Metal Concentrations, Summitville Mine Area, Upper Alamosa River Basin, Southwest Colorado, 1995–97

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CONVERSION FACTORS, VERTICAL DATUM, ACRONYMS, AND ABBREVIATED WATER-QUALITY UNITS

Multiply	By	To obtain
acre	0.4047	hectare
acre-foot (acre-ft)	1,233	cubic meter
cubic foot per second (ft^3/s)	0.02832	cubic meter per second
foot (ft)	0.3048	meter
inch	25.4	millimeter
mile (mi)	1.609	kilometer
miles per hour (mi/h)	1.609	kilometers per hour
square mile (mi^2)	2.590	square kilometer

Degree Celsius (°C) may be converted to degree Fahrenheit (°F) by using the following equation:

$$°F = 9/5\ °C + 32$$

Degree Fahrenheit (°F) may be converted to degree Celsius (°C) by using the following equation:

$$°C = 5/9\ (°F - 32)$$

Sea level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

Additional acronyms and site identifiers:

AR45.5	Alamosa River above Wightman Fork
AR41.2	Alamosa River below Jasper
AR34.5	Alamosa River above Terrace Reservoir
AR31.0	Alamosa River below Terrace Reservoir
EWI	Equal width increment
EA	Exposure area
WF5.5	Wightman Fork below Cropsy Creek
WFO.0	Wightman Fork at mouth

Abbreviated water-quality units:

mg/L	milligrams per liter
µg/L	micrograms per liter

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Abstract

The upper Alamosa River Basin contains areas that are geochemically altered and have associated secondary sulfide mineralization. Occurring with this sulfide mineralization are copper, gold, and silver deposits that have been mined since the 1870's. Weathering of areas with sulfide mineralization produces runoff with anomalously low pH and high metal concentrations; mining activities exacerbate the condition. Summer rainstorms in the upper Alamosa River Basin produce a characteristic relation between streamflow and pH; streamflow suddenly increases and pH suddenly decreases (commonly by more than 1 pH unit). This report evaluates changes in pH in the upper Alamosa River Basin during July, August, and September 1995, 1996, and 1997 to examine possible adverse environmental effects due to rainstorm runoff.

Ninety-three percent of the rainstorms occurring during 1995–97 produced runoff throughout the entire basin. Out of 54 storms, only 3 storms were isolated to the river reach upstream from the streamflow-gaging station Alamosa River above Wightman Fork, and only 1 storm was isolated to the river reach between the streamflow-gaging stations Alamosa River below Jasper and Alamosa River above Terrace Reservoir.

Although most rainstorm runoff events occurred throughout the entire basin, pH changes were highest in parts of the basin that receive runoff from hydrothermally altered areas. The three principal altered areas within the basin are the Jasper, Stunner, and Summitville areas. Only limited mining occurred in the Stunner altered area, and yet significant decreases in pH values occur due to runoff from this area. Even after environmental restoration activities are completed at the Summitville Mine, the main stem of the Alamosa River may continue to be adversely affected by runoff from the Stunner and Jasper altered areas.

A comparison of measured pH with Federal and State of Colorado water-quality standards and Toxicological Reference Values indicates pH was too low to support aquatic life in many parts of the basin for extended periods of time. Added stresses from sudden decreases in pH due to rainstorm runoff compound the adverse effects.

Discharge of effluent from the Summitville Mine impoundment can significantly decrease pH in the Alamosa River downstream to Terrace Reservoir. A release of only 3 cubic feet per second from the impoundment decreased pH by at least 1 standard unit at all downstream sites.

Low-flow years may pose a substantial risk to aquatic organisms within and downstream from Terrace Reservoir. During 1996, the basin had a low-flow year, and water storage and pool size of Terrace Reservoir were significantly reduced. The pH of water discharging from Terrace Reservoir was anomalously low during late August and September 1996, possibly due to geochemical

interactions between sediment and the water column within the reservoir.

In general, an inverse log-log relation exists between pH and the logarithm of dissolved metal concentrations, but the relations generally are not significant enough to confidently predict metal concentrations based upon measured pH values.

INTRODUCTION

The Summitville Mine area of the upper Alamosa River Basin in Colorado (fig. 1) has been mined for copper, gold, and silver since the 1870's. Most mining operations at Summitville were on a relatively small scale until the mid-1980's, when mining operations were expanded to include a large open-pit cyanide heap leach operation (Pendleton and others, 1995). Cyanide and acid solutions were inadvertently discharged to Wightman Fork on numerous occasions during the late 1980's and early 1990's. Mining operations also exposed sulfide minerals to oxygen, causing acid-mine drainage and elevated metal concentrations in ground water and surface water at the mine site (Pendleton and others, 1995). In December 1992, the mining company declared bankruptcy and the U.S. Environmental Protection Agency (USEPA) initiated an Emergency Response Action to help reduce environmental effects from the mine. Since that time, the Summitville mine was declared a Superfund site and the USEPA and the Colorado Department of Public Health and Environment (CDPHE) have been taking remedial actions at the mine to help reduce adverse environmental effects.

Mining operations at Summitville are only one source of low pH and high metal concentrations in the Alamosa River Basin upstream from Terrace Reservoir (upper Alamosa River Basin). Significant natural sources of contaminants are Iron, Alum, Jasper, and Burnt Creeks. Kirkham and others (1995) inventoried 219 mine openings and 130 mine dumps in the upper Alamosa River Basin, and estimated that nearly 11 percent of the iron, 18 percent of the aluminum, and 1 percent of the copper, manganese, and zinc in surface water upstream from the confluence of the Alamosa River with Wightman Fork are supplied by abandoned mines. The balance of these dissolved metals is from natural sources. Miller and McHugh (1994) identified five major altered areas in and adjacent to the upper Alamosa River Basin. Three of those altered areas are shown in figure 1.

Mining operations in the upper Alamosa River Basin, particularly at the Summitville Mine, are implicated in the elimination of trout populations in the Alamosa River and Terrace Reservoir. In 1889, the Alamosa River was known as a trout stream that contained Rio Grande cutthroat trout (Woodling, 1995). As early as 1974, negative effects from acid-mine drainage in the upper Alamosa River Basin were identified (Wentz, 1974). By 1985, the Rio Grande cutthroat had disappeared; however, reproducing brook trout were reported in an Alamosa River headwater reach (Woodling, 1995). From 1960 through 1990, Terrace Reservoir was stocked with fingerling rainbow trout, which grew to catchable size and were harvested by anglers (Woodling, 1995). In the mid-1980's, the open-pit cyanide heap leach operation at Summitville, Colorado, was opened. Discharges from the facility increased the metal concentrations (primarily copper) in Wightman Fork and the Alamosa River downstream from the confluence with Wightman Fork. In June 1990, a fishkill in a privately owned pond supplied with irrigation water from the Alamosa River was confirmed by the Colorado Division of Wildlife (CDOW). On July 12, 1990, the CDOW concluded that no fish existed in Terrace Reservoir (Woodling, 1995). The copper concentration in the Alamosa River upstream from Terrace Reservoir was 1,270 μg/L (micrograms per liter) on June 23, 1990, compared to a concentration of 30 μg/L in 1986. The rainbow trout 96-hour LC50 for copper (the concentration that will kill 50 percent of the test organisms in 4 days) is 52 μg/L.

Ortiz and others (1995) observed that the pH significantly decreased and dissolved metals significantly increased in response to localized rainstorms in the upper Alamosa River Basin. Therefore, a study was conducted during 1999 by the U.S. Geological Survey (USGS), in cooperation with the USEPA, to evaluate the relations among rainstorm runoff, streamflow, pH, and metal concentrations. Information from the study is intended to assist in the evaluation of acute and chronic effects of rainstorm runoff on pH in the Alamosa River and its tributaries. This evaluation provided information for the Draft Tier II Summitville Ecological Risk Assessment that the USEPA developed for the Summitville Superfund site.

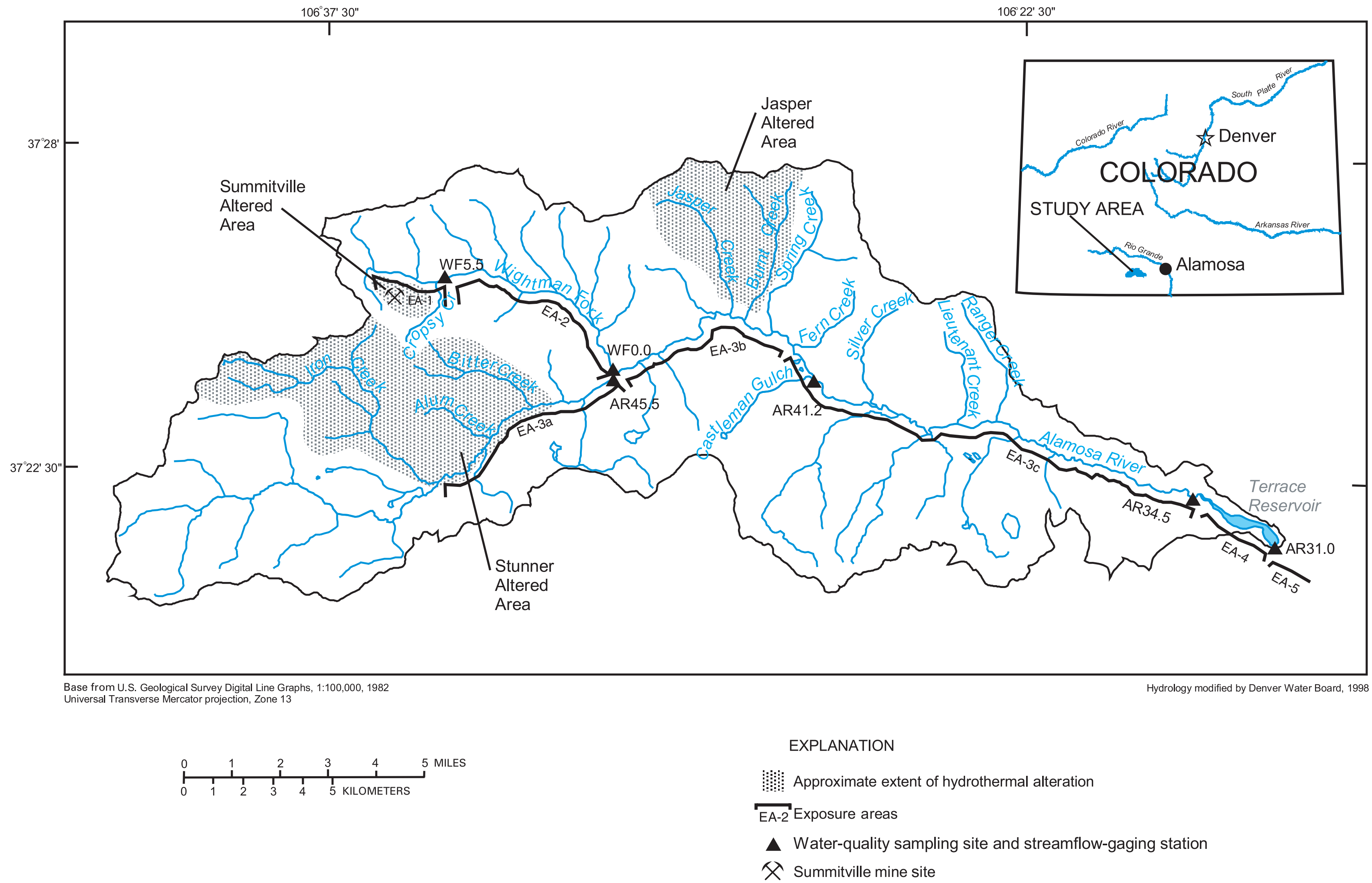

Figure 1. Locations of study area, exposure areas, and water-quality sampling sites in the Alamosa River Basin.

Purpose and Scope

The purpose of this report is to describe the relations among rainstorm runoff, streamflow, pH, and metal concentrations at six streamflow-gaging stations in the upper Alamosa River Basin. These stations (fig. 1, table 1) are: (1) Wightman Fork below Cropsy Creek (WF5.5, USGS station number 08235270), (2) Wightman Fork at mouth (WF0.0, USGS station number 08235290), (3) Alamosa River above Wightman Fork (AR45.5, USGS station number 08235250), (4) Alamosa River below Jasper (AR41.2, USGS Station number 08235700), (5) Alamosa River above Terrace Reservoir (AR34.5; USGS Station number 08236000), and (6) Alamosa River below Terrace Reservoir (AR31.0, USGS station number 08236500). The relations of streamflow and pH were based on data collected by continuous water-quality monitors during July 1 through September 30, 1995, 1996, and 1997. The relations of dissolved metal concentrations and pH were based on nonstorm and storm samples collected during water years 1994–97 (water years begin on October 1 and end on September 30 and are designated by the calendar year in which they end). Annual precipitation data were evaluated for water years 1995, 1996, and 1997. Annual variations of precipitation in the basin were evaluated to examine their relation to rainstorm runoff and pH. Rainstorms occurring in different parts of the basin were evaluated to quantify effects due to runoff in those parts of the basin. The effects of discharge of effluent from an impoundment at the Summitville Mine was evaluated to observe pH changes in Wightman Fork and the Alamosa River. The pH values measured in Wightman Fork and the Alamosa River were compared to water-quality standards to evaluate potential effects on aquatic biota.

Study Area Description

The upper Alamosa River Basin is in southwest Colorado (fig. 1). Elevations in the study area range from nearly 13,000 ft above sea level for the highest mountains to 8,400 ft near Terrace Reservoir. Annual precipitation ranges from approximately 40 inches in the highest mountains to approximately 12 inches near Terrace Reservoir (Miller and McHugh, 1994). Most of the high-elevation precipitation is in the form of snow.

The upper Alamosa River Basin extends from the Alamosa River headwaters to just downstream from Terrace Reservoir and has a drainage area of approximately 116 mi^2. Terrace Reservoir stores water leaving the basin and serves as a trap for sediments. When constructed in 1912, Terrace Reservoir had a surface area of 300 acres and a storage capacity of approximately 8,110 acre-ft (Watts, 1996).

The upper Alamosa River Basin is located in the southeastern portion of the San Juan volcanic field (Bove and others, 1995). The bedrock is composed mostly of rhyolitic ash-flow deposits associated with the formation of the Platoro caldera complex. The bedrock of several areas in the basin is hydrothermally altered and contains sulfide minerals and precious metals. These altered areas (fig. 1) are identified easily in the field as tan and red bleached landscapes and are the ancient analogues of the active geyser basins at Yellowstone National Park in Wyoming (Bove and others, 1995). Runoff from mined areas and from

Table 1. Upper Alamosa River Basin streamflow-gaging station numbers, site identifiers, station names, elevations, and drainage areas

[Exposure areas are segments of the basin that are being assessed in an Ecological Risk Assessment of the U.S. Environmental Protection Agency; mi^2, square miles]

USGS station number	Site identifier	Exposure area	Station name	Approximate elevation (feet above sea level)	Drainage area (mi^2)
08235270	WF5.5	Exposure Area 1	Wightman Fork below Cropsy Creek	11,090	4.44
08235290	WF0.0	Exposure Area 2	Wightman Fork at mouth	9,380	16.1
08235250	AR45.5	Exposure Area 3a	Alamosa River above Wightman Fork	9,380	37.8
08235700	AR41.2	Exposure Area 3b	Alamosa River below Jasper	9,030	76.3
08236000	AR34.5	Exposure Area 3c	Alamosa River above Terrace Reservoir	8,610	107
08236500	AR31.0	Exposure Area 5	Alamosa River below Terrace Reservoir	8,380	116

unmined altered areas adversely affects water quality and pH in the Alamosa River and its tributaries. Bove and others (1995) measured specific conductance and pH at more than 60 sites and observed a good correlation between the type and intensity of alteration and the degree to which surface water and spring water are degraded. The presence of old iron-oxide-cemented conglomerates many feet above modern streams indicates the generation of natural metal-rich, acidic drainage has been occurring for many thousands of years prior to mining in the area (Bove and others, 1995).

The bedrock was altered through a complex series of geologic processes. The South Mountain volcanic dome was formed about 22.4 million years ago (Plumlee and others, 1995). As part of the dome-forming cycle, additional magmatic material was intruded in the area beneath the dome. As the magmas crystallized, they released hot gases rich in sulfur dioxide. The gases rose along fractures and eventually condensed, producing fluids rich in sulfuric acid that extensively leached and altered the bedrock. Following the period of intense acid leaching, copper- and gold-rich sulfide minerals were deposited in the highly altered dome rocks by hot hydrothermal fluids also derived from crystallizing magmas at depth (Plumlee and others, 1995). Sulfide minerals such as pyrite (FeS_2), marcasite (FeS_2), and enargite (Cu_3AsS_4) were deposited in these highly altered zones. Subsequent erosion exposed these sulfide minerals to well-oxygenated surface water and ground water, resulting in runoff with anomalously low pH values and anomalously high metal concentrations. Open-pit mining at Summitville exposed large quantities of sulfide minerals to oxygenated waters, creating adverse environmental effects much greater than those naturally occurring.

Acid-mine drainage is produced primarily by the oxidation of the mineral pyrite (FeS_2). Pyrite oxidation is a complex process (Nordstrom and Alpers, 1999) that proceeds rapidly when pyrite and other sulfide minerals are exposed to oxygen and oxygenated water. Pyrite reacts with oxygen and water to form ferrous sulfate and sulfuric acid. The dissolved ferrous iron continues to oxidize and hydrolyze when the mine water is no longer in contact with pyrite, producing additional acidity. Iron- and sulfur-oxidizing bacteria are known to increase reaction rates by several orders of magnitude (Nordstrom and Alpers, 1999). Acidic drainage occurs naturally in many locations in the upper Alamosa River Basin. Mining at Summitville substantially increased the oxidation rates by providing greater accessibility of air and oxygenated water through mine workings, waste rock, and tailings.

The USEPA has subdivided the upper Alamosa River Basin into five river reaches, which are termed Exposure Areas (EA) (fig. 1). These EAs were defined to enhance the ability to summarize environmental effects on biota within specific river reaches. These EAs were evaluated in the Draft Tier II Summitville Ecological Risk Assessment. Site WF5.5 is located at the downstream end of EA-1 and serves as a water-quality indicator site for EA-1. Site WF0.0 is a water-quality indicator site for EA-2, AR45.5 is a water-quality indicator site for EA-3a, AR41.2 is a water-quality indicator site for EA-3b, AR34.5 is a water-quality indicator site for EA-3c, and AR31.0 is a water-quality indicator site for EA-5 (fig. 1, table 1).

Methods of Investigation

Stream-stage and pH were measured at six streamflow-gaging stations. Stream-stage data were measured every 15 minutes, and pH was measured every 30 minutes. These data were transferred by satellite and stored in the National Water Information System (NWIS) database operated and maintained by the USGS. Stream-stage data were converted to streamflow data by the NWIS database by using the stage/discharge relation established at each site. These data are available for download directly from the NWIS database (contact District Chief, U.S Geological Survey, Box 25046, Mail Stop 415, Denver Federal Center, Denver, CO, 80225–0046). For this study, streamflow and pH data for 30-minute increments during July 1 through September 30, 1995, 1996, and 1997 were analyzed using a variety of geographic-information-system, graphing, spreadsheet, and statistical software.

Relations between pH and selected dissolved-metal concentrations were evaluated by this study. There were insufficient data to specifically evaluate the effects of pH decreases on metal concentrations during storm events because only a subset of samples were collected during rainstorm runoff. To compile enough data for analysis, all dissolved-metal data collected throughout water years 1994–97 were used. Generally, composites of six samples in a 24-hour period were collected during the months of April through September. Because flow conditions were relatively stable in the fall and winter, equal width increment (EWI) grab samples were collected during October through March.

Rainstorm runoff events were identified by observing streamflow records. Runoff events were identified when instantaneous streamflow increased at least 10 percent during a 1-hour period. Events identified using this method correlated well with daily precipitation data that have been collected since December 1992 at the Summitville Mine by USEPA contractors.

ANNUAL AND SEASONAL VARIATION OF PRECIPITATION, RUNOFF, AND STREAMFLOW

Annual and seasonal variations in precipitation affected streamflow in the upper Alamosa River Basin. Annual precipitation totals at the Summitville Mine for water years 1995, 1996, and 1997 were 41.78, 17.12, and 72.81 inches, respectively. Water year 1996 was much drier than water years 1995 and 1997, and precipitation in the summer months of 1996 also was much less than in the summer months of 1995 and 1997. July through September precipitation totals for 1995, 1996, and 1997 were l3.44, 7.24, and 14.66 inches, respectively. The smaller amount of precipitation during water year 1996 is reflected in streamflow, where minimum, median, and maximum streamflows at all sites were much smaller in 1996 (table 2) than in 1995 or 1997.

Annual and seasonal variations of precipitation in the upper Alamosa River Basin affected the magnitude and duration of rainstorm runoff. The number of rainstorm runoff events that occurred between July 1 and September 30 was 17 in 1995, 18 in 1996, and 19 in 1997. Although the number of runoff events was about the same each year, the magnitudes and durations differed among the three years. The changes in streamflow (difference between prestorm and peak flows) in 1996 were significantly less at all sites than in 1995 and 1997 (fig. 2). For instance, median changes in streamflow at AR45.5 due to rainstorm runoff were 30 ft^3/s in 1995, 7.8 ft^3/s in 1996, and 42.5 ft^3/s in 1997 (table 3). Smaller changes in streamflow due to rainstorm runoff reflect the overall drier conditions in the summer of 1996.

The duration of change in streamflow due to rainstorm runoff on the main stem of the Alamosa River tended to be longer in 1996 than in 1995 and 1997 (fig. 2; AR45.5, AR41.2, AR34.5). The generally longer durations of change in 1996 were related to less water in the Alamosa River; streamflow velocities were slower, and a longer time was needed for the peak streamflow to travel through the drainage system. The duration of change in streamflow tended to be less in 1996 at WF5.5 and WF0.0 possibly because of the much smaller drainage areas (table 1).

RELATIONS AMONG RAINSTORM RUNOFF, STREAMFLOW, pH, AND METAL CONCENTRATIONS

Several factors affect streamflow, pH, and metal concentrations in the upper Alamosa River Basin. The following text evaluates the effects of rainstorm runoff on streamflow and pH, the effects of annual variations in streamflow on pH, the effects of rainstorms occurring in different parts of the basin, the effects of discharge of effluent from the Summitville Mine impoundment, the variations in pH of water discharging from Terrace Reservoir, a comparison of pH values to water-quality standards, and the relation between pH and metal concentrations.

Effects of Rainstorm Runoff on Streamflow and pH

Rainstorm runoff in the upper Alamosa River Basin generally produces a characteristic relation between streamflow and pH. Generally, when streamflow increases due to rainstorm runoff, pH immediately decreases (fig. 3). Typically, when the rainstorm runoff ends, streamflow decreases to approximately near the prestorm discharge, and pH increases to approximately near the prestorm value. The sudden decrease in pH is probably due to runoff from hydrothermally altered areas (fig. 1) that are enriched in sulfide minerals. Between rainstorms, sulfide minerals in the soil and bedrock can oxidize. This oxidation can lower the pH and increase the metal concentrations in the sediments and interstitial water. When rainstorms occur in the oxidized areas, the runoff can carry the products of oxidized sulfide minerals into the drainage

Table 2. Statistical summary of streamflow and pH at selected sites in the upper Alamosa River Basin, southwest Colorado, during July, August, and September 1995, 1996, and 1997

[WF5.5, Wightman Fork below Cropsy Creek; WF0.0, Wightman Fork at mouth; AR45.5, Alamosa River above Wightman Fork; AR41.2, Alamosa River below Jasper; AR34.5, Alamosa River above Terrace Reservoir; AR31.0, Alamosa River below Terrace Reservoir]

Year	WF5.5	WF0.0	AR45.5	AR41.2	AR34.5	AR31.0
Minimum streamflow, in cubic feet per second						
1995	1.6	3.6	32	39	30	67.9
1996	0.6	1.2	6.3	10.4	19	11.8
1997	2.8	4.4	31	35	45	38.5
Median streamflow, in cubic feet per second						
1995	6.7	12	61	91	104	177
1996	2.1	3.5	13	21.6	35	57
1997	6.1	11.7	59	81.9	91	100
All 3 years	4.7	9.1	44	62	73	87.5
Maximum streamflow, in cubic feet per second						
1995	51	164	218	889	920	812
1996	27	41	161	194	224	141
1997	30	79	236	350	464	290
Minimum pH, in standard units						
1995	3.0	3.1	3.7	2.7	4.4	4.7
1996	2.8	3.4	3.0	3.4	4.1	4.3
1997	2.8	3.2	3.5	4.3	4.7	5.2
Median pH, in standard units						
1995	3.6	4.3	5.9	4.8	5.6	5.6
1996	4.6	5.5	4.9	5.4	6.8	6.6
1997	4.1	4.9	6.5	5.9	6.7	6.7
All 3 years	4.1	4.9	6.0	5.3	6.5	6.2
Maximum pH, in standard units						
1995	4.6	4.9	7.0	6.1	6.3	6.6
1996	6.7	6.6	7.2	7.0	7.3	7.1
1997	5.0	6.4	7.3	6.9	7.2	7.2

system, causing a decrease in the pH and an increase in the metal concentrations in local streams.

An example of the effects of rainstorm runoff on pH in the upper Alamosa River Basin is provided by data collected on August 30–31, 1997 (fig. 3), when a rainstorm produced runoff throughout the basin. As the streamflow increased, the pH immediately decreased at all sites. At AR45.5, the streamflow nearly doubled from about 40 ft^3/s to about 80 ft^3/s; at the same time the pH decreased from about 6.5 to about 4.7. After the rainstorm, streamflow and pH returned to approximately the same values as before the rainstorm. As the peak streamflow moved downstream, the durations of the peak streamflow increased and the pH decreases were progressively longer. These longer durations may be the result of the stream water mixing with water from different parts of the basin.

The pH generally increases in a downstream direction (fig. 3, graph showing pH at all stations), probably as a result of dilution by runoff from unaltered areas. The increase probably does not occur as a result of reactions with materials in the stream channel because the bedrock in the downstream area is composed mostly of silicic volcanic rocks that have little buffering capacity. Also, the altered areas are located in the upper two-thirds of the basin (fig. 1), and runoff in the lower one-third of the basin is not affected by altered areas. Ward and Walton-Day (1995) observed that most dissolved-metal concentrations decrease and pH increases in a downstream direction. They indicated the changes in water quality

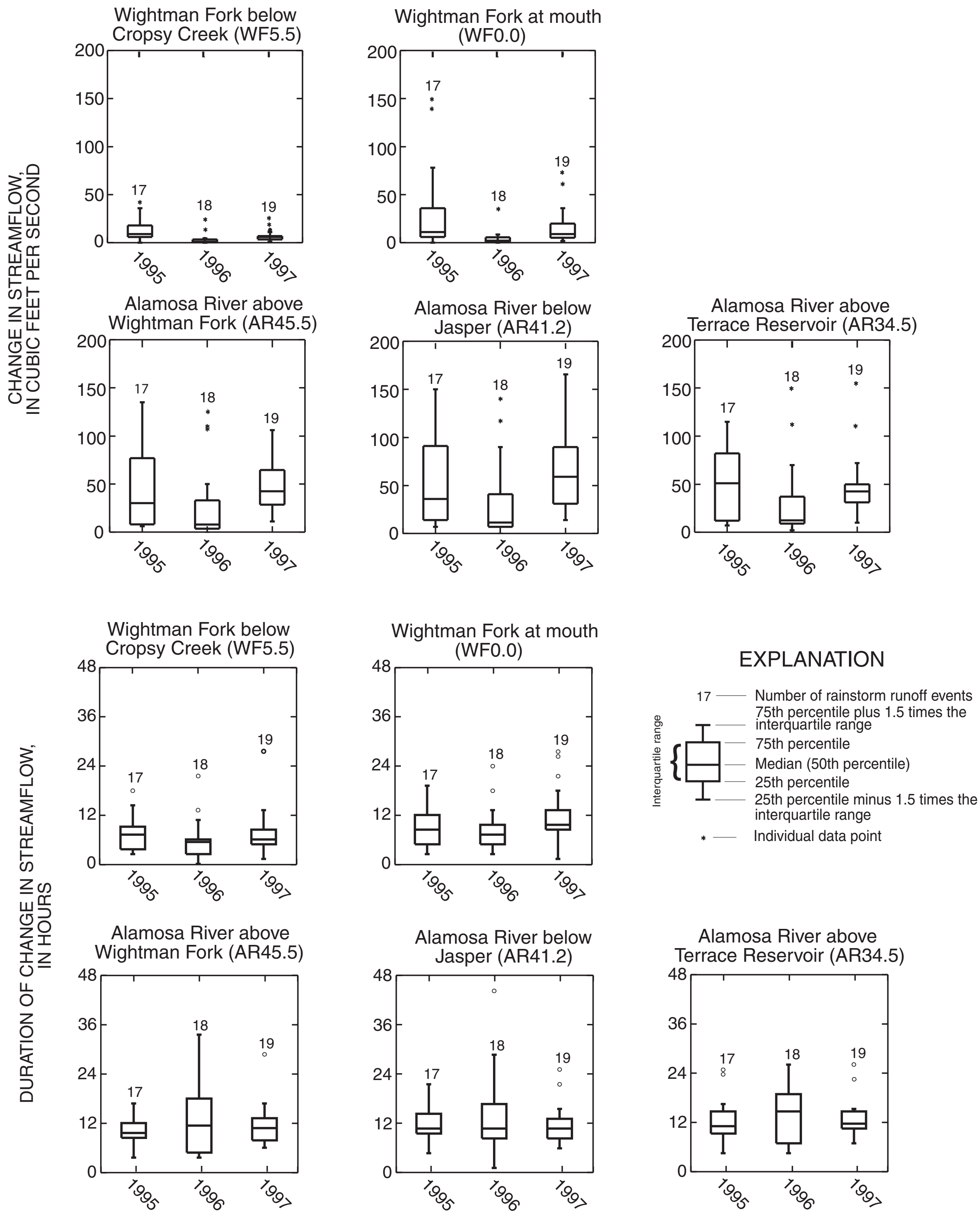

Figure 2. Change and duration of change in streamflow due to rainstorm runoff at selected sites, upper Alamosa River Basin, southwest Colorado, 1995–97.

Table 3. Statistical summary of changes in streamflow and pH due to rainstorm runoff at selected sites in the upper Alamosa River Basin, southwest Colorado, during July, August, and September 1995, 1996, and 1997

[WF5.5, Wightman Fork below Cropsy Creek; WF0.0, Wightman Fork at mouth; AR45.5, Alamosa River above Wightman Fork; AR41.2, Alamosa River below Jasper; AR34.5, Alamosa River above Terrace Reservoir]

Year	WF5.5	WF0.0	AR45.5	AR41.2	AR34.5
Minimum change in streamflow, in cubic feet per second					
1995	0	0	6	7	7
1996	0	0	2	0	2
1997	1	1.9	11	14	10
Median change in streamflow, in cubic feet per second					
1995	9	11	30	36	51
1996	.9	2.2	7.8	11.5	12.5
1997	5.8	9	42.5	60	43
All 3 years	4.5	7	30	41	37
Maximum change in streamflow, in cubic feet per second					
1995	42	150	135	150	115
1996	24	36	126	140	150
1997	25	72	200	310	260
Minimum change in pH, in standard units					
1995	0	0	.1	.1	0
1996	0	0	0	0	0
1997	.2	.1	0	0	0
Median change in pH, in standard units					
1995	.3	.3	.8	.25	.4
1996	.9	.9	1	.6	.6
1997	.8	.3	1.7	.5	.6
All 3 years	.3	.4	1	.5	.5
Maximum change in pH, in standard units					
1995	.6	.9	1.6	1	.9
1996	1.9	2.3	2.7	2.5	2.8
1997	1.5	1.2	3.1	2	1.7

may be due to dilution or natural reactions (such as mineral precipitation and sorption) but stated additional data were needed for verification.

Relative streamflow is shown in figure 3 to illustrate how the peak streamflow moves through the basin; the magnitudes of streamflow at each site were made relative to each other in this graph to highlight the traveltime of the peak streamflow through the basin. For the rainstorm on August 30–31, 1997, approximately 0.3 day (approximately 7.2 hours) was needed for the peak streamflow to travel from AR45.5 to AR34.5 (approximately 14.1 miles), with an approximate velocity of 2 mi/h. A statistical summary of the traveltimes of peak streamflow and the low-pH front throughout the basin for July through September in 1995, 1996, and 1997 is given in table 4.

Effects of Annual Variations in Streamflow on pH

The effects of annual variations in July through September precipitation on pH were evaluated. Minimum, median, and maximum pH had no apparent systematic relation to annual variations in streamflow (table 2). However, at most sites, the changes in pH (difference between prestorm and peak values) tended to be larger in 1996 than in 1995 and 1997 (table 3, fig. 4), presumably because of less water in the system (table 2) and, thus, less water available for dilution. It is unknown why the change in pH at AR45.5 was larger in 1997 (fig. 4). It also is unknown how the drier conditions in 1996 affected the pH of soils and interstitial water in the altered areas that are likely sources for low-pH waters in the basin.

With the exception of AR34.5, the variation in duration of change in pH due to rainstorm runoff between 1995, 1996, and 1997 was small (table 5, fig. 4). At AR34.5, the duration of change due to rainstorm runoff in 1996 was substantially longer. This longer duration of pH decrease could be detrimental to any aquatic life in the river.

The traveltimes of peak streamflow and the low-pH front as the peak moved through the basin also were calculated (table 4, fig. 5). Median traveltimes of peak streamflow and the pH front were slightly longer in 1996, presumably because of the lower streamflow that year.

Rainstorms in Different Parts of the Basin and Their Effects on Streamflow and pH

Ninety-three percent of the rainstorms identified using streamflow records produced runoff throughout the entire basin. During 1995–97, 54 rainstorms occurred, but only 3 storms were isolated to the reach upstream from AR45.5 and only 1 storm was isolated to the reach between AR41.2 and AR34.5.

Large decreases in pH were measured at AR45.5 during the three rainstorms that were isolated to the reach upstream from that site (table 6). These decreases ranged from 1 to 2.5 standard units and were thought to be due to runoff from the Stunner altered area (fig. 1). The pH decreased as much as 2.6 units at AR4l.2. For the most part, the pH was close to neutral

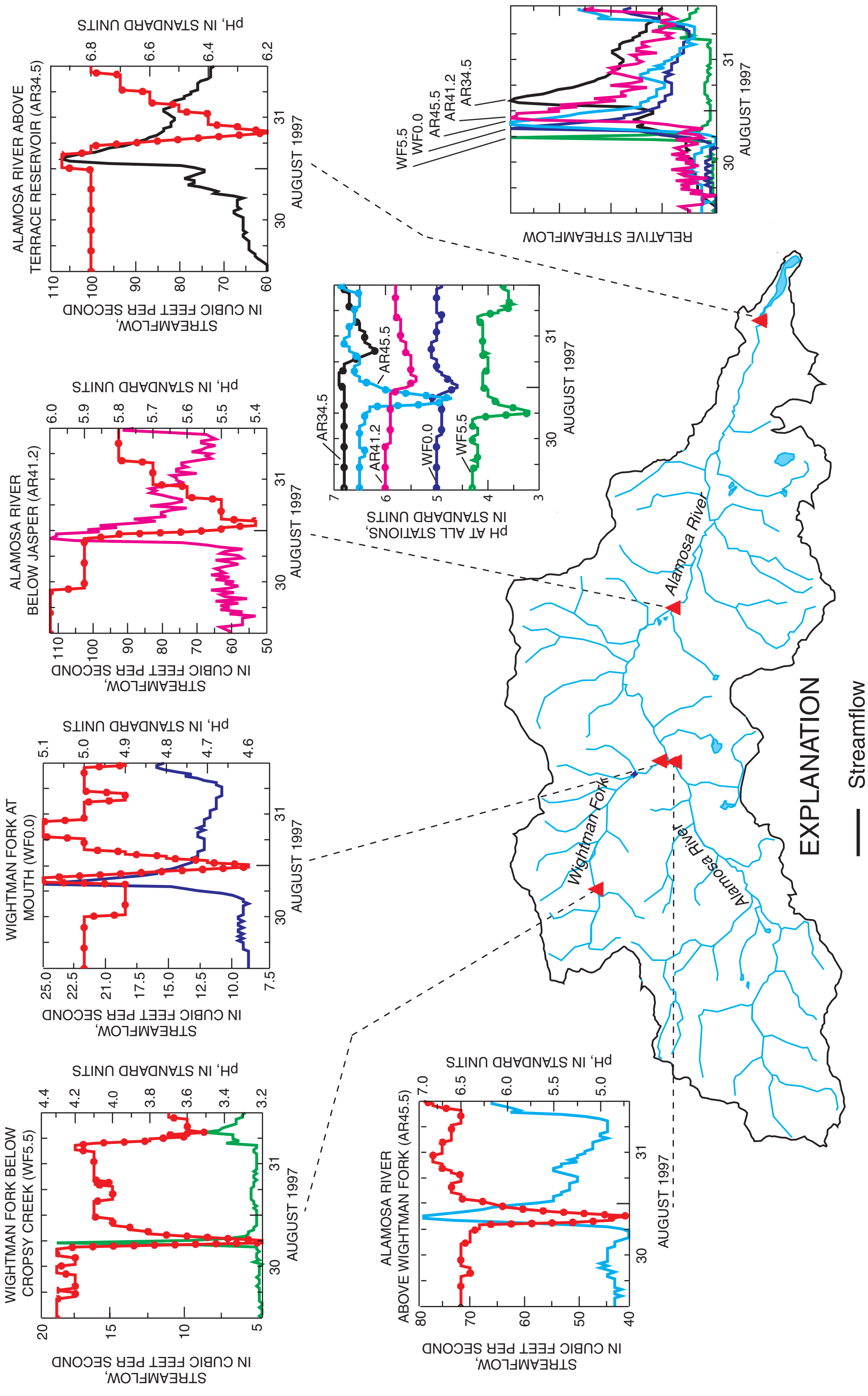

Figure 3. Streamflow and pH, August 30–31, 1997, upper Alamosa River Basin, southwest Colorado.

Table 4. Statistical summary of traveltimes of peak streamflow and low-pH front through selected segments of the Alamosa River and Wightman Fork, upper Alamosa River Basin, southwest Colorado, during July, August, and September 1995, 1996, and 1997

[WF5.5, Wightman Fork below Cropsy Creek; WF0.0, Wightman Fork at mouth; AR45.5, Alamosa River above Wightman Fork; AR41.2, Alamosa River below Jasper; AR34.5, Alamosa River above Terrace Reservoir; h, hour]

Year	WF5.5 to WF0.0	AR45.5 to AR41.2	AR45.5 to AR34.5
Minimum traveltime of peak streamflow, in decimal days			
1995	0.05 (1.2 h)	0.05 (1.2 h)	0.10 (2.4 h)
1996	.05 (1.2 h)	.05 (1.2 h)	.05 (1.2 h)
1997	.05 (1.2 h)	.05 (1.2 h)	.10 (2.4 h)
Median traveltime of peak streamflow, in decimal days			
1995	.10 (2.4 h)	.10 (2.4 h)	.25 (6 h)
1996	.10 (2.4 h)	.10 (2.4 h)	.30 (7.2 h)
1997	.10 (2.4 h)	.10 (2.4 h)	.25 (6 h)
All 3 years	.10 (2.4 h)	.10 (2.4 h)	.25 (6 h)
Maximum traveltime of peak streamflow, in decimal days			
1995	.20 (4.8 h)	.45 (10.8 h)	.70 (16.8 h)
1996	.35 (8.4 h)	.20 (4.8 h)	.55 (13.2 h)
1997	.15 (3.6 h)	.25 (6 h)	.35 (8.4 h)
Minimum traveltime of low-pH front, in decimal days			
1995	.05 (1.2 h)	.05 (1.2 h)	.15 (3.6 h)
1996	.05 (1.2 h)	.05 (1.2 h)	.15 (3.6 h)
1997	.05 (1.2 h)	.10 (2.4 h)	.10 (2.4 h)
Median traveltime of low-pH front, in decimal days			
1995	.20 (4.8 h)	.18 (4.3 h)	.33 (7.9 h)
1996	.25 (6 h)	.20 (4.8 h)	.40 (9.6 h)
1997	.15 (3.6 h)	.15 (3.6 h)	.35 (8.4 h)
All 3 years	.20 (4.8 h)	.18 (4.3 h)	.35 (8.4 h)
Maximum traveltime of low-pH front, in decimal days			
1995	.50 (12 h)	.50 (12 h)	1.4 (33.6 h)
1996	.50 (12 h)	.45 (10.8 h)	1.2 (28.8 h)
1997	.55 (13.2 h)	.30 (7.2 h)	.50 (12 h)

by the time the peak streamflow reached AR34.5, but decreases in pH still occurred (table 6).

Only one rainstorm was isolated in the lowermost part of the basin. The small rainstorm caused a 10 ft^3/s (50 percent) increase in streamflow at AR34.5, but pH remained the same (6.3). No rainstorm-related changes in streamflow or pH occurred at any of the other sites. The lack of change in pH during the rainstorm runoff event suggests this part of the basin does not contribute significant low-pH runoff. No altered areas exist in this segment of the basin (fig. 1, EA-3c).

These results suggest that isolated rainstorms occurring downstream from Fern Creek (fig. 1) probably pose little risk of anomalously low pH. However, isolated rainstorms occurring in the upper Alamosa River Basin upstream from the confluence with Wightman Fork pose a substantial risk of contributing anomalously low pH runoff to the main stem of the Alamosa River, which can affect pH values in the Alamosa River for several miles downstream.

Effects of Untreated Discharge from the Summitville Mine Impoundment

There is an impoundment at the Summitvllle Mine which is used to capture and hold acid-mine drainage from the mine site. The impoundment waters have low pH values and high metal concentrations; the median pH value measured from May 1997 through October 1997 was 3.1 and the median dissolved copper concentration was 30,000 µg/L (Bruce Marshall, Rocky Mountain Consultants, written commun., 1999), which is more than 500 times the 96-hour LC50 reported for rainbow trout. The impoundment waters are pumped to a treatment plant where the pH is raised and a large portion of the metal load is removed. The treated water then is discharged to Wightman Fork. However, sometimes untreated effluent from the impoundment has been discharged directly to Wightman Fork, such as during the mid- to late summer months of 1997 (July 10–12, July 23–25, August 7–8, and August 10–12) (Bruce Marshall, Rocky Mountain Consultants, written commun., 1999). Releases on August 7–8 and August 10–12 coincided with rainstorms, so the effects of the releases of untreated effluent on Wightman Fork and the Alamosa River could not be quantified; however, releases on July 10–12 (fig. 6) and July 23–25 occurred at times of no precipitation.

Release of effluent from the Summitville Mine impoundment affects pH at all sites downstream from WF5.5 (fig. 6). At approximately 8:30 a.m. on July 10, 1997, untreated effluent was released from the impoundment. This release increased the streamflow at WF5.5 from about 8 ft^3/s to about 11 ft^3 /s and decreased the pH from 4.2 to 3.2 (fig. 6). The release

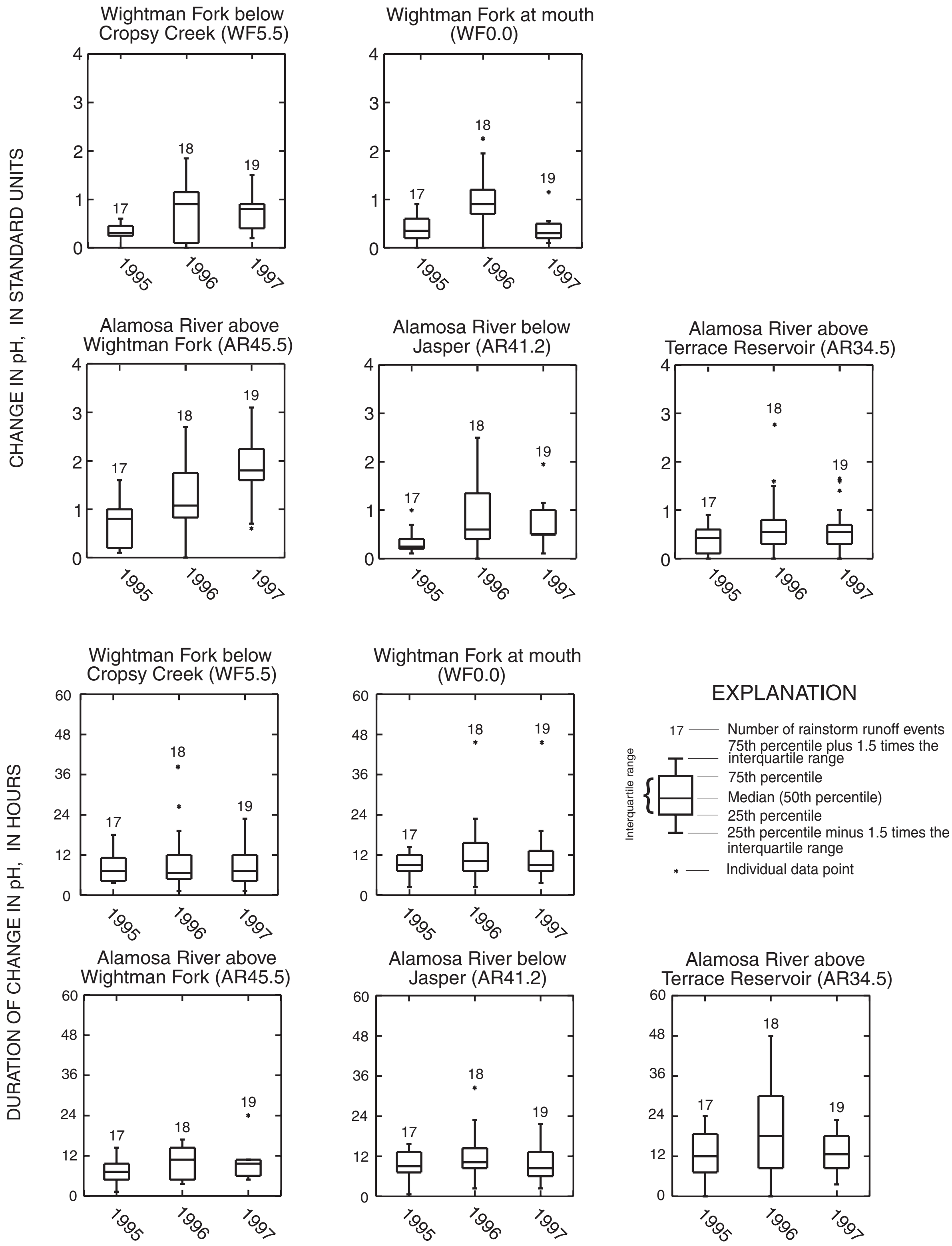

Figure 4. Change and duration of change in pH due to rainstorm runoff at selected sites, upper Alamosa River Basin, southwest Colorado, 1995–97.

Table 5. Statistical summary of duration of changes in streamflow and pH due to rainstorm runoff at selected sites in the upper Alamosa River Basin, southwest Colorado, during July, August, and September 1995, 1996, and 1997

[WF5.5, Wightman Fork below Cropsy Creek; WF0.0, Wightman Fork at mouth; AR45.5, Alamosa River above Wightman Fork; AR41.2, Alamosa River below Jasper; AR34.5, Alamosa River above Terrace Reservoir; %, percent; h, hour]

Year	WF5.5	WF0.0	AR45.5	AR41.2	AR34.5
			Minimum duration of change in streamflow, in decimal days		
1995	0.10 (2.4 h)	0.10 (2.4 h)	0.15 (3.6 h)	0.20 (4.8 h)	0.20 (4.8 h)
1996	.10 (2.4 h)	.10 (2.4 h)	.15 (3.6 h)	.05 (1.2 h)	.20 (4.8 h)
1997	.05 (1.2 h)	.05 (1.2 h)	.25 (6 h)	.25 (6 h)	.10 (2.4 h)
			Median duration of change in streamflow, in decimal days		
1995	.3 (7.2 h)	.35 (8.4 h)	.40 (9.6 h)	.45 (10.8 h)	.48 (11.5 h)
1996	.23 (5.5 h)	.30 (7.2 h)	.48 (11.5 h)	.45(10.8 h)	.63 (15.1 h)
1997	.25 (6 h)	.40 (9.6 h)	.45 (10.8 h)	.45 (10.8 h)	.50 (12 h)
			Maximum duration of change in streamflow, in decimal days		
1995	.75 (18 h)	.80 (19.2 h)	.70 (16.8 h)	.90 (21.6 h)	1.10 (26.4 h)
1996	.90 (21.6 h)	1.00 (24 h)	1.40 (33.6 h)	1.80 (43.2 h)	2.80 (67.2 h)
1997	1.15 (27.6 h)	1.20 (28.8 h)	1.20 (28.8 h)	1.05 (25.2 h)	1.10 (26.4 h)
			Minimum duration of change in pH, in decimal days		
1995	.15 (3.6 h)	.10 (2.4 h)	.05 (1.2 h)	.03 (0.7 h)	.10 (2.4 h)
1996	.05 (1.2 h)	.10 (2.4 h)	.15 (3.6 h)	.10 (2.4 h)	.10 (2.4 h)
1997	.05 (1.2 h)	.15 (3.6 h)	.20 (4.8 h)	.10 (2.4 h)	.15 (3.6 h)
			Median duration of change in pH, in decimal days		
1995	.30 (7.2 h)	.38 (9.1 h)	.30 (7.2 h)	.38 (9.1 h)	.50 (12 h)
1996	.28 (6.7 h)	.43 (10.3 h)	.45(10.8 h)	.43 (10.3 h)	.75 (18 h)
1997	.30 (7.2 h)	.38 (9.1 h)	.40 (9.6 h)	.35 (8.4 h)	.53 (12.7 h)
			Maximum duration of change in pH, in decimal days		
1995	.75 (18 h)	.60 (14.4 h)	.60 (14.4 h)	.65 (15.6 h)	1.00 (24 h)
1996	1.60 (38.4 h)	1.90 (45.6 h)	.70 (16.8 h)	1.35 (32.4 h)	2.00 (48 h)
1997	.95 (22.8 h)	1.90 (45.6 h)	1.00 (24 h)	.90 (21.6 h)	.95 (22.8 h)
			Number and percentage of rainstorms causing decreased pH values for greater than 4 hours		
1995	13 (76%)	16 (94%)	14 (82%)	15 (88%)	15 (88%)
1996	15 (83%)	17 (94%)	16 (89%)	17 (94%)	17 (94%)
1997	14 (74%)	18 (95%)	19 (100%)	18 (95%)	18 (95%)
			Number and percentage of rainstorms causing decreased pH values for greater than 96 hours		
1995	0 (0%)	0 (0%)	0 (0%)	0 (0%)	0 (0%)
1996	0 (0%)	0 (0%)	0 (0%)	0 (0%)	0 (0%)
1997	0 (0%)	0 (0%)	0 (0%)	0 (0%)	0 (0%)

increased the streamflow at WF0.0 by about the same amount (3 ft^3/s) and decreased the pH from 5 to about 3.7. This release occurred in mid-July when snowmelt was still contributing to streamflow in the Alamosa River. Data from AR45.5 demonstrate a relation between streamflow and pH that is characteristic of snowmelt runoff; the streamflow displays a diurnal fluctuation, and pH closely mimics the variation in streamflow due to dilution by snowmelt (fig. 6). The diurnal fluctuations in streamflow are still apparent at AR41.2, but the diurnal fluctuations in pH are diminished. Instead, pH decreased by more than 1 standard unit due to the release of untreated effluent from the impoundment. Apparently, the untreated effluent was highly concentrated because the streamflow of Wightman Fork increased by only 3 ft^3/s, and yet the pH at AR41.2, which had streamflow values ranging from approximately 95 ft^3/s to approximately 135 ft^3/s, decreased by more than 1 unit. Data for AR34.5 demonstrated relations similar to those at

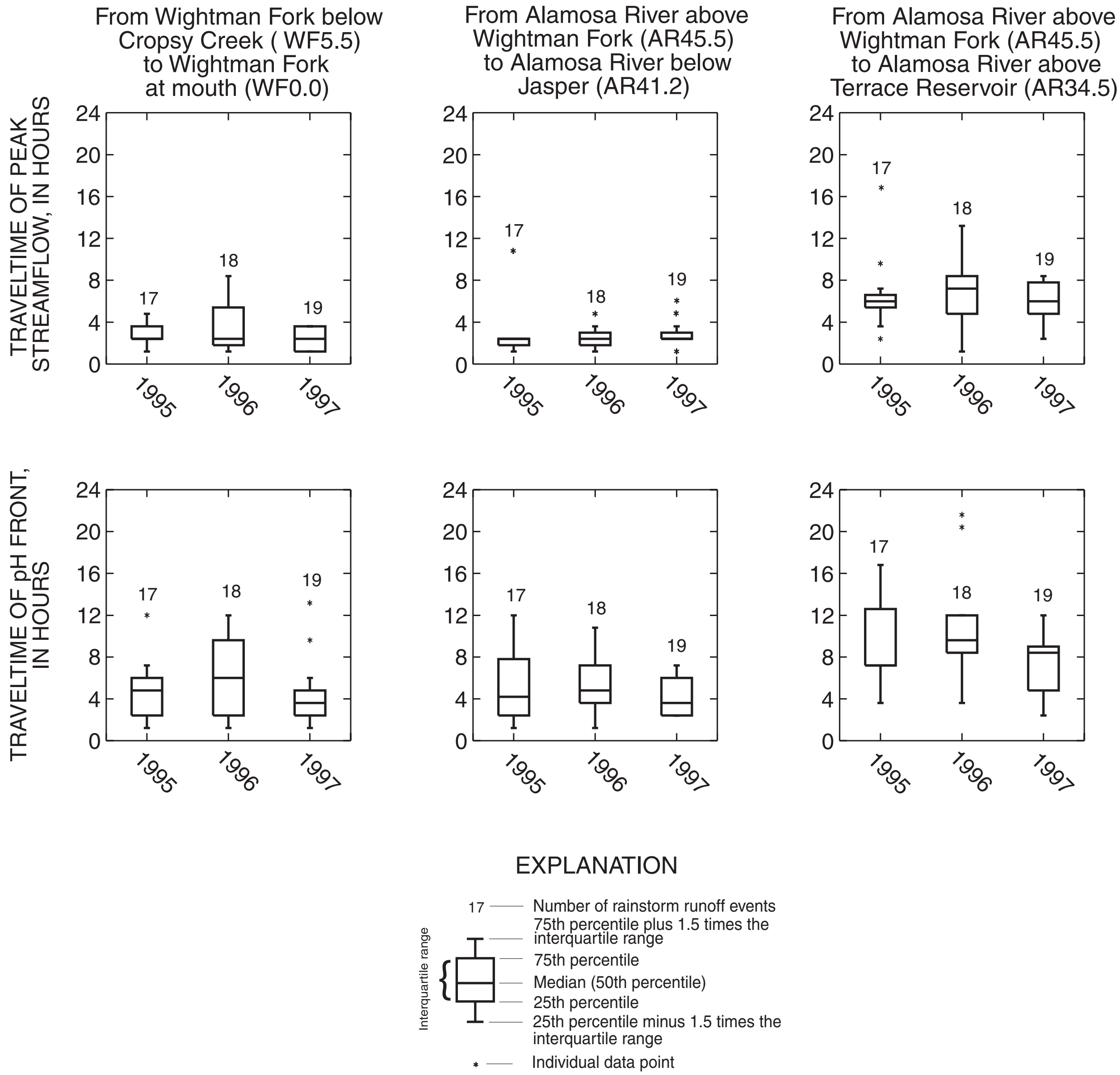

Figure 5. Traveltimes of peak streamflow and low-pH front through selected segments of the Alamosa River and Wightman Fork, upper Alamosa River Basin, southwest Colorado, 1995–97.

AR41.2; streamflow was more than 100 ft^3/s, but pH decreased by more than 1 unit due to the release of untreated effluent from the impoundment.

Based upon data from July 10–12, 1997, and July 23–25, 1997 (which showed conditions similar to those described above), release of untreated effluent from the Summitville Mine impoundment may significantly decrease pH in the Alamosa River as far downstream as Terrace Reservoir.

Variations in pH of Water Discharging from Terrace Reservoir

The pH of water in, and discharging from, Terrace Reservoir during low-flow years may pose a significant risk to aquatic organisms. During the summer of 1996, the upper Alamosa River Basin had relatively low streamflow (table 2). Water storage and pool size of Terrace Reservoir also were relatively low; during August 1996, the storage was only

Table 6. Changes in streamflow and pH due to rainstorms isolated to the reach upstream from the Alamosa River above Wightman Fork station during July, August, and September 1995, 1996, and 1997, upper Alamosa River Basin, southwest Colorado

[AR45.5, Alamosa River above Wightman Fork; AR41.2, Alamosa River below Jasper; AR34.5, Alamosa River above Terrace Reservoir; EA, exposure area; Q-begin, streamflow before rainstorm; Q-max, maximum streamflow due to rainstorm; pH-begin, pH value before rainstorm; pH-min, minimum pH value due to rainstorm]

Date	Q-begin	Q-max	pH-begin	pH-min
		AR45.5		
9/01/95	45	53	6.2	5.2
7/12/96	40	90	6.5	4.5
7/25/96	20	31	6.5	4.0
		AR41.2		
9/01/95	66	73	4.6	4.4
7/12/96	72	123	6.7	5.7
7/25/96	30	42	6.3	3.7
		AR34.5		
9/01/95	67	74	6.2	6.1
7/12/96	90	136	7.2	6.7
7/25/96	46	55	7.2	5.7

2,091 acre-ft. In comparison, storage was 5,572 acre-ft during August 1997 (Craig Cotten, Colorado Department of Water Resources, written commun., 1999). During August 21–29, 1996, the upper basin received a series of relatively low-intensity, long-duration rainstorms. Shortly after the start of these rainstorms, pH at AR34.5 began a decrease from about 6.3 to about 4.7 on August 22, l996 (fig. 7). Approximately 38 hours later, pH at AR31.0 began a decrease from about 6.7 to about 4.8. The distance between AR34.5 and AR3l.0 is approximately 4.3 miles, so the travel velocity of the pH front through the reservoir was about 0.1 mi/h. On September 2, the pH at AR34.5 increased to about 6.5, but the pH at AR31.0 remained less than 5.8 until near the end of September. During September 12–25, the basin also had several small rainstorms, and streamflow at AR34.5 ranged from about 25 ft^3/s to more than 40 ft^3/s. During this time, pH at AR34.5 was never less than 6.0, but pH at AR31.0 ranged from about 4.3 to 5.4.

It is unclear why the pH remained anomalously low at AR3l.0 for such a long period of time, even though the pH at AR34.5 returned to more than 6.0. Geochemical interactions between sediment and the water column within the reservoir are a possible cause of the low pH. Water in the reservoir is well oxygenated and has limited microbial activity, so the most likely reactions or processes that can occur in the reservoir include oxidation and precipitation of ferric hydroxides, adsorption and desorption of metals, complexation of dissolved metals with ligands, and flocculation (Stogner and others, 1997). Ferric hydroxide formation is plausible and would help explain why the pH at AR3l.0 was lower than the pH at AR34.5. Horowitz and others (1996, p. 6) substantiated the possibility of ferric hydroxide formation; they reported the bottom of the reservoir to be covered by a thin (0.25- to 1.2-inch), soupy, fine-grained, red-orange floc that they believed to contain large quantities of ferric hydroxide. Stogner and others (1997) noted that pH tended to decrease and metal concentrations tended to increase in a downstream direction in Terrace Reservoir. However, Stogner and others (1997, p. 21) suggested that oxidation and chemical precipitation of metal hydroxides probably were not dominant processes in the reservoir because most of the ferric hydroxide probably formed in the river upstream from the reservoir. A possible explanation may be that the relatively low water levels in Terrace Reservoir during the summer of 1996 allowed reservoir sediments to be exposed to the atmosphere and to be reworked due to downcutting by the Alamosa River, allowing for additional metal hydroxide formation. Regardless of the cause, these relations indicate that pH in the reservoir may remain significantly lowered following rainstorm runoff during low-flow years, thus hampering efforts to improve water quality. Additional study would be useful to help determine if geochemical interactions between the sediment and water column within Terrace Reservoir may hamper restoration of the reservoir and downstream reaches to fishable status, even after remediation efforts at the Summitville Mine are completed.

Comparison of pH Values to Water-Quality Standards and Toxicological Reference Values

The USEPA has established quality criteria for water for many constituents (U.S. Environmental Protection Agency, 1986). The freshwater chronic exposure criterion, which is long-term exposure under ambient conditions (not just storm events), for pH is 6.5 to 9.0 standard units. At all sites examined in this

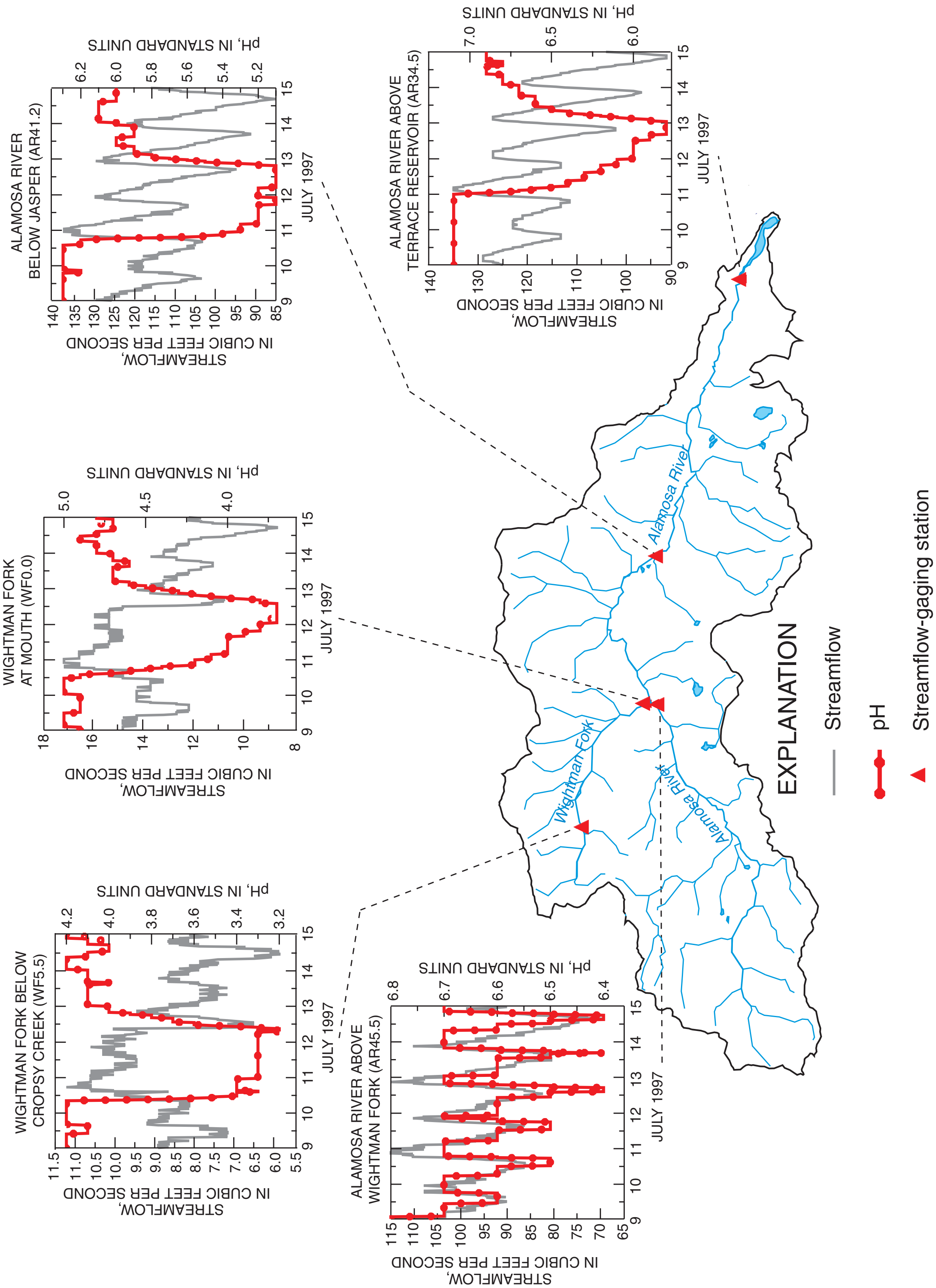

Figure 6. Streamflow and pH during July 9–15, 1997, upper Alamosa River Basin, southwest Colorado.

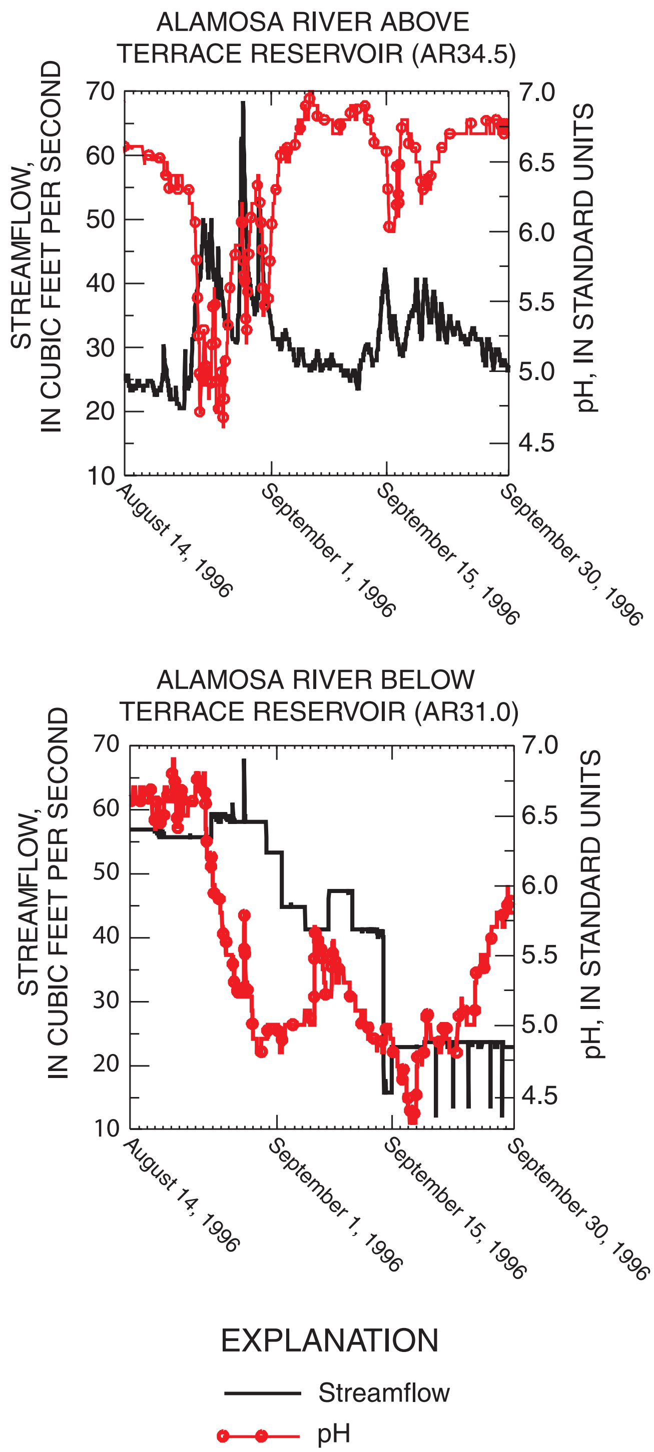

Figure 7. Streamflow and pH at Alamosa River above Terrace Reservoir and Alamosa River below Terrace Reservoir, August 14 through September 30, 1996, upper Alamosa River Basin, southwest Colorado.

study, the pH was below 6.5 for extended periods of time (table 2, table 7, figs. 8–13). This indicates pH in many parts of the upper Alamosa River Basin do not meet the USEPA pH standard for aquatic life.

The State of Colorado has established water-quality standards for most stream segments in the Alamosa River drainage (Colorado Department of Public Health and Environment, 1998). The water-quality standard for pH on the river segment near AR45.5 (EA-3a) varies depending on the time of year (fig. 10). Colorado water-quality standards for pH were exceeded on numerous occasions at AR45.5 and were exceeded continuously during most of August 1996 (fig. 10). Colorado standards for pH were not established for the stream segments where WF5.5 and WF0.0 (EA-2) are located, but the Federal standard of 6.5 was rarely met (figs. 8–9, table 7). The Colorado

Table 7. Percentage of pH measurements that did not meet Colorado and Federal water-quality standards and Toxicological Reference Values during July, August, and September 1995, 1996, and 1997, upper Alamosa River Basin, southwest Colorado

[Measurements taken every 30 minutes during July, August, and September; WF5.5, Wightman Fork below Cropsy Creek; WF0.0, Wightman Fork at mouth; AR45.5, Alamosa River above Wightman Fork; AR41 2, Alamosa River below Jasper; AR34.5, Alamosa River above Terrace Reservoir; AR3 1.0, Alamosa River below Terrace Reservoir; TRV; Toxicological Reference Value; ne, standard not established]

Year	WF5.5	WF0.0	AR45.5	AR41.2	AR34.5	AR31.0
Percentage of pH measurements less than Federal water-quality standard (pH 6.5)						
1995	100	100	77	100	100	100
1996	99	98	87	86	23	44
1997	100	100	39	85	25	20
Percentage of pH measurements less than Colorado water-quality standard (pH standard depends on specific reach)						
1995	ne	ne	1	100	100	100
1996	ne	ne	42	86	23	44
1997	ne	ne	1	85	25	20
Percentage of pH measurements less than TRV for chronic exposure, benthic macroinvertebrates (pH = 6.5)						
1995	100	100	77	100	100	100
1996	99	98	87	86	23	44
1997	100	100	52	85	25	20
Percentage of pH measurements less than TRV for acute exposure, benthic macroinvertebrates (pH = 5.38)						
1995	100	100	22	99	31	35
1996	95	39	71	48	5	30
1997	100	91	4	16	5	1
Percentage of pH measurements less than TRV for chronic exposure, adult rainbow trout (pH = 5.6)						
1995	100	100	29	99	47	47
1996	96	56	73	58	6	35
1997	100	96	7	24	5	5
Percentage of pH measurements less than TRV for acute exposure, adult rainbow trout (pH = 4.2)						
1995	97	46	1	1	0	0
1996	24	2	5	1	1	0
1997	54	7	1	0	0	0

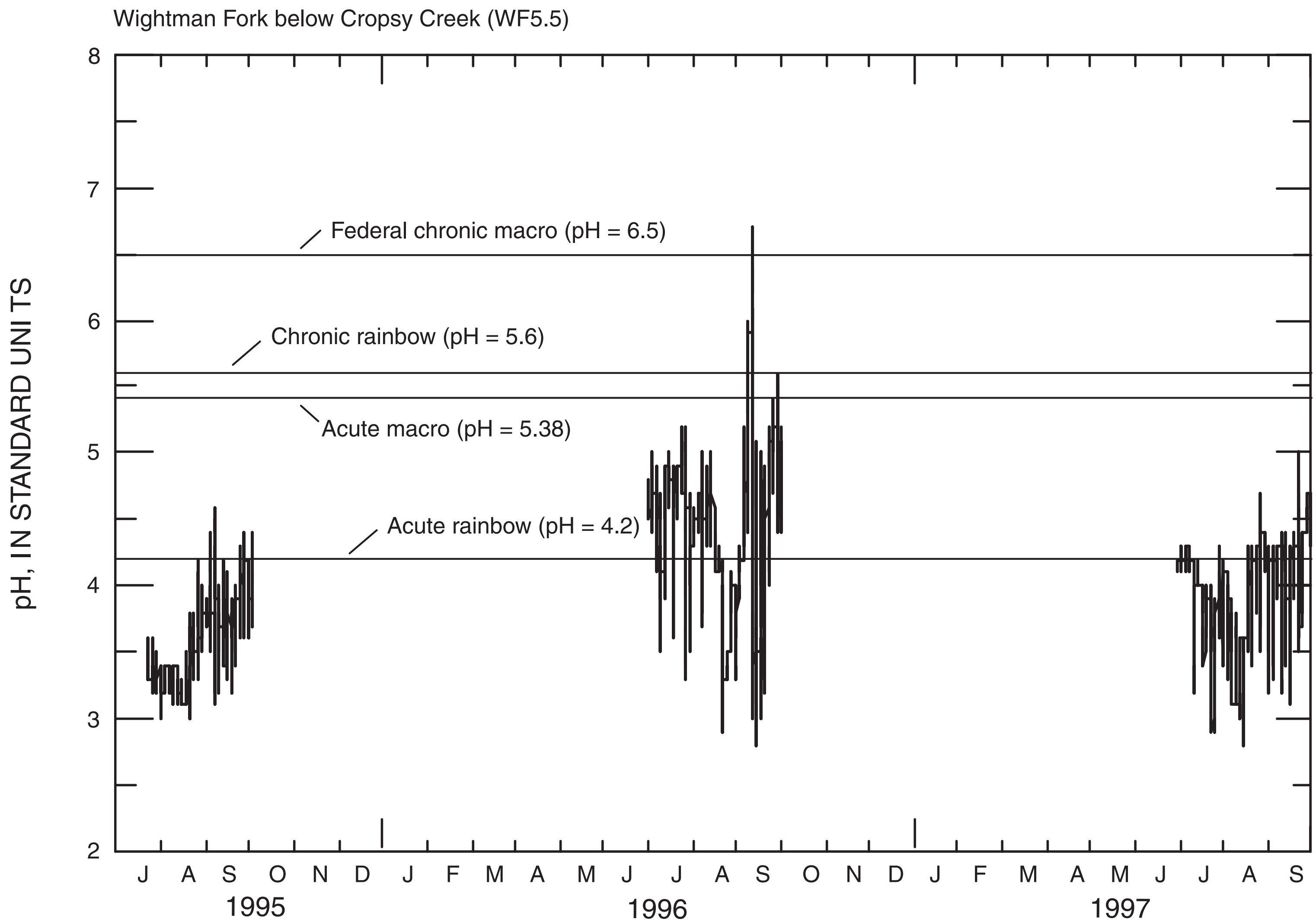

Figure 8. Federal water-quality standards, Toxicological Reference Values, and pH at Wightman Fork below Cropsy Creek (WF5.5), upper Alamosa River Basin, July 1, 1995, through September 30, 1997. [TRV, Toxicological Reference Value, Federal chronic macro, Federal water-quality standard and chronic TRV for benthic macroinvertebrates, pH = 6.5; chronic rainbow, chronic TRV for adult rainbow trout, pH = 5.6; acute macro, acute TRV for benthic macroinvertebrates, pH = 5.38; acute rainbow, acute TRV for adult rainbow trout, pH = 4.2]

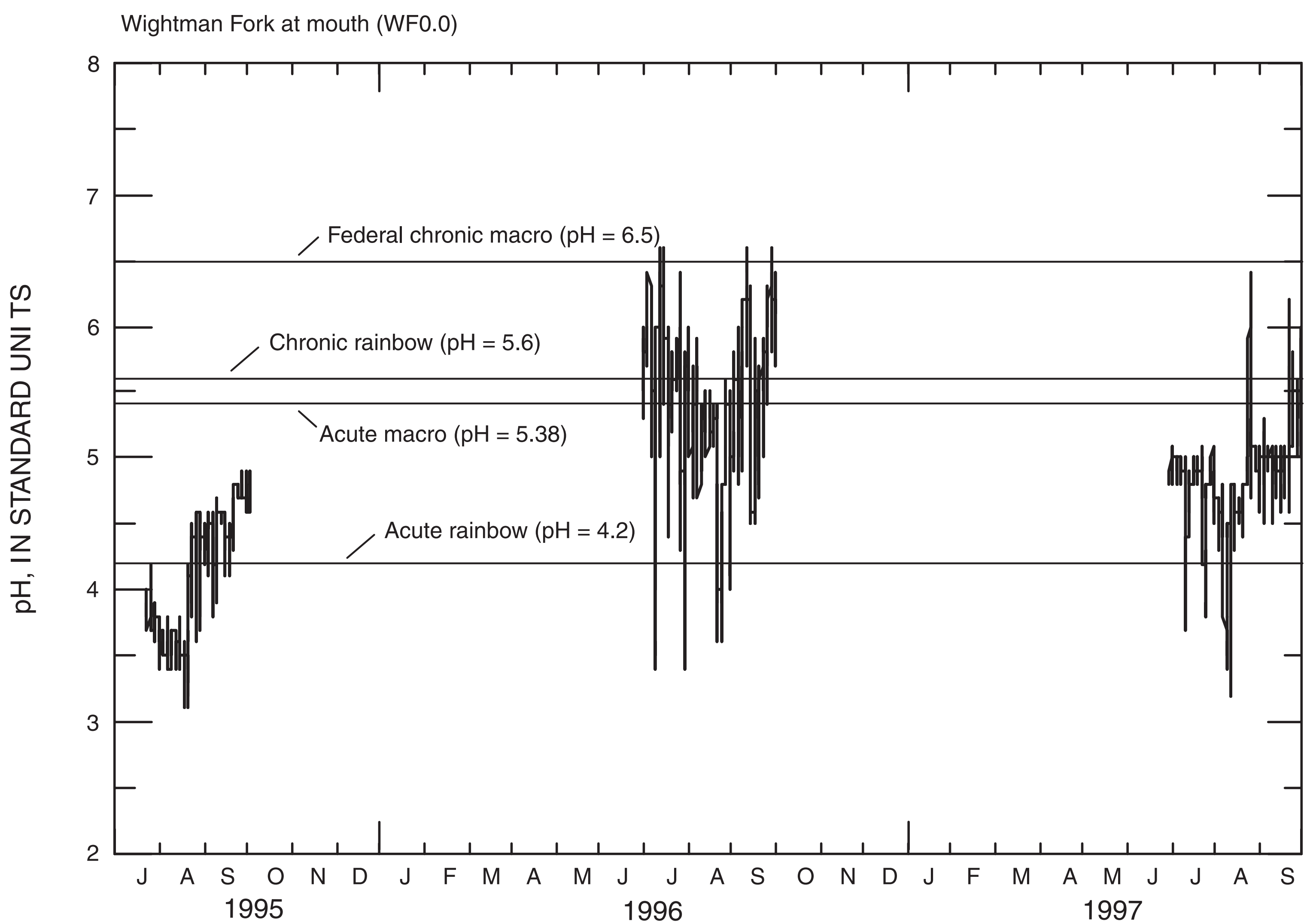

Figure 9. Federal water-quality standards, Toxicological Reference Values and pH at Wightman Fork at mouth (WF0.0), upper Alamosa River Basin, July 1, 1995, through September 30, 1997. [TRV, Toxicological Reference Value; Federal chronic macro, Federal water-quality standard and chronic TRV for benthic macroinvertebrates, pH = 6.5; chronic rainbow, chronic TRV for adult rainbow trout, pH = 5.6; acute macro, acute TRV for benthic macroinvertebrates, pH = 5.38; acute rainbow, acute TRV for adult rainbow trout, pH = 4.2]

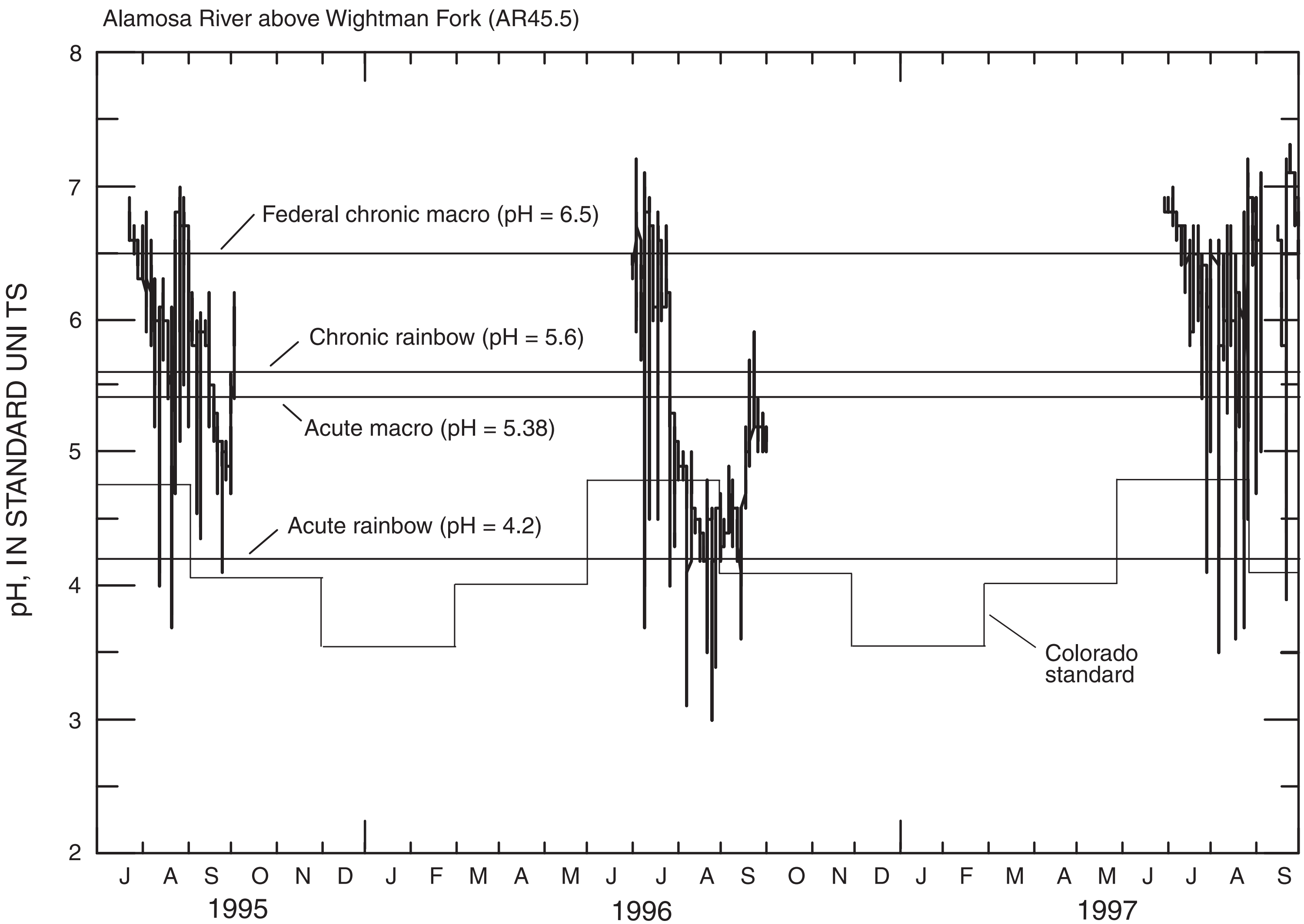

Figure 10. Colorado and Federal water-quality standards, Toxicological Reference Values, and pH at Alamosa River above Wightman Fork (AR45.5), upper Alamosa River Basin, July 1, 1995, through September 30, 1997. [TRV, Toxicological Reference Value; Federal chronic macro, Federal water-quality standard and chronic TRV for benthic macroinvertebrates, pH = 6.5; chronic rainbow, chronic TRV for adult rainbow trout, pH = 5.6; acute macro, acute TRV for benthic macroinvertebrates, pH = 5.38; acute rainbow, acute TRV for adult rainbow trout, pH = 4.2; Colorado, Colorado water-quality standard for pH, varies depending on time of year]

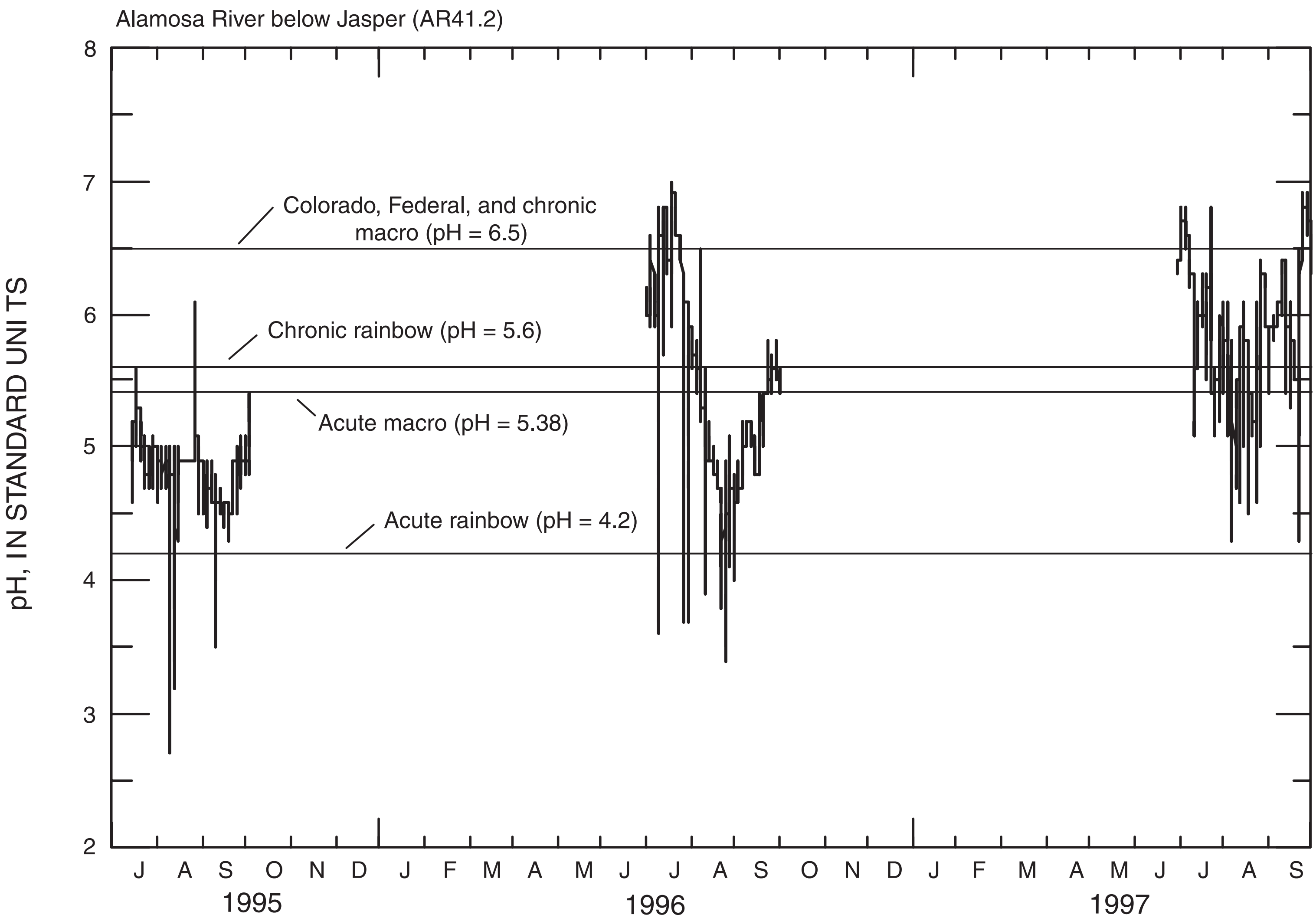

Figure 11. Colorado and Federal water-quality standard, Toxicological Reference Values, and pH at Alamosa River below Jasper (AR41.2), upper Alamosa River Basin, July 1, 1995, through September 30, 1997. [TRV, Toxicological Reference Value; Colorado, Colorado water-quality standard, pH = 6.5; Federal, Federal water-quality standard, pH = 6.5; chronic macro, chronic TRV for benthic macroinvertebrates, pH = 6.5; chronic rainbow, chronic TRV for adult rainbow trout, pH = 5.6; acute macro, acute TRV for benthic macroinvertebrates, pH = 5.38; acute rainbow, acute TRV for adult rainbow trout, pH = 4.2]

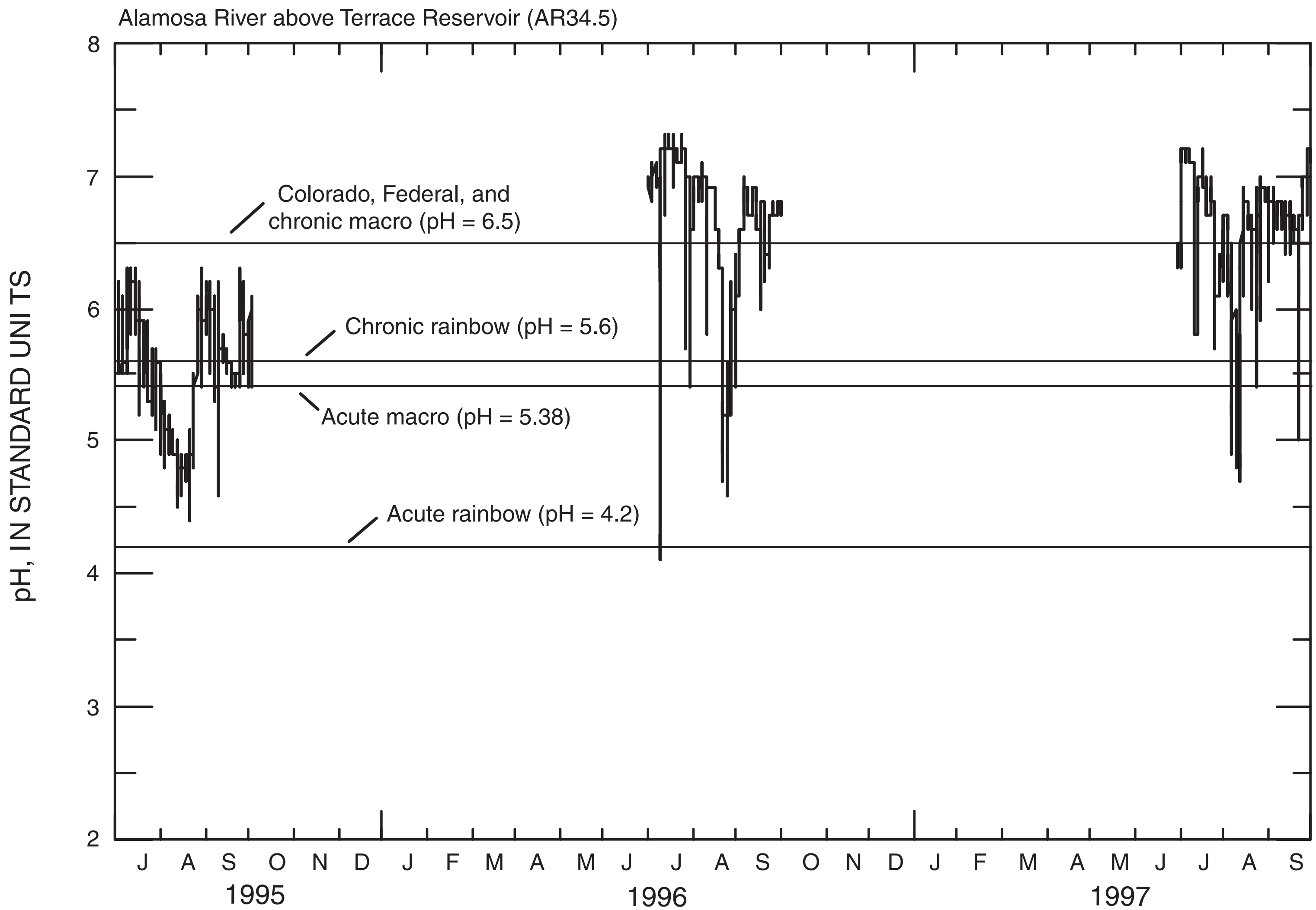

Figure 12. Colorado and Federal water-quality standards, Toxicological Reference Values, and pH at Alamosa River above Terrace Reservoir (AR34.5), upper Alamosa River Basin, July 1, 1995, through September 30, 1997. [TRV, Toxicological Reference Value; Colorado, Colorado water-quality standard, pH = 6.5; Federal, Federal water-quality standard, pH = 6.5; chronic macro, chronic TRV for benthic macroinvertebrates, pH = 6.5; chronic rainbow, chronic TRV for adult rainbow trout, pH = 5.6; acute macro, acute TRV for benthic macroinvertebrates, pH = 5.38p acute rainbow, acute TRV for adult rainbow trout, pH = 4.2]

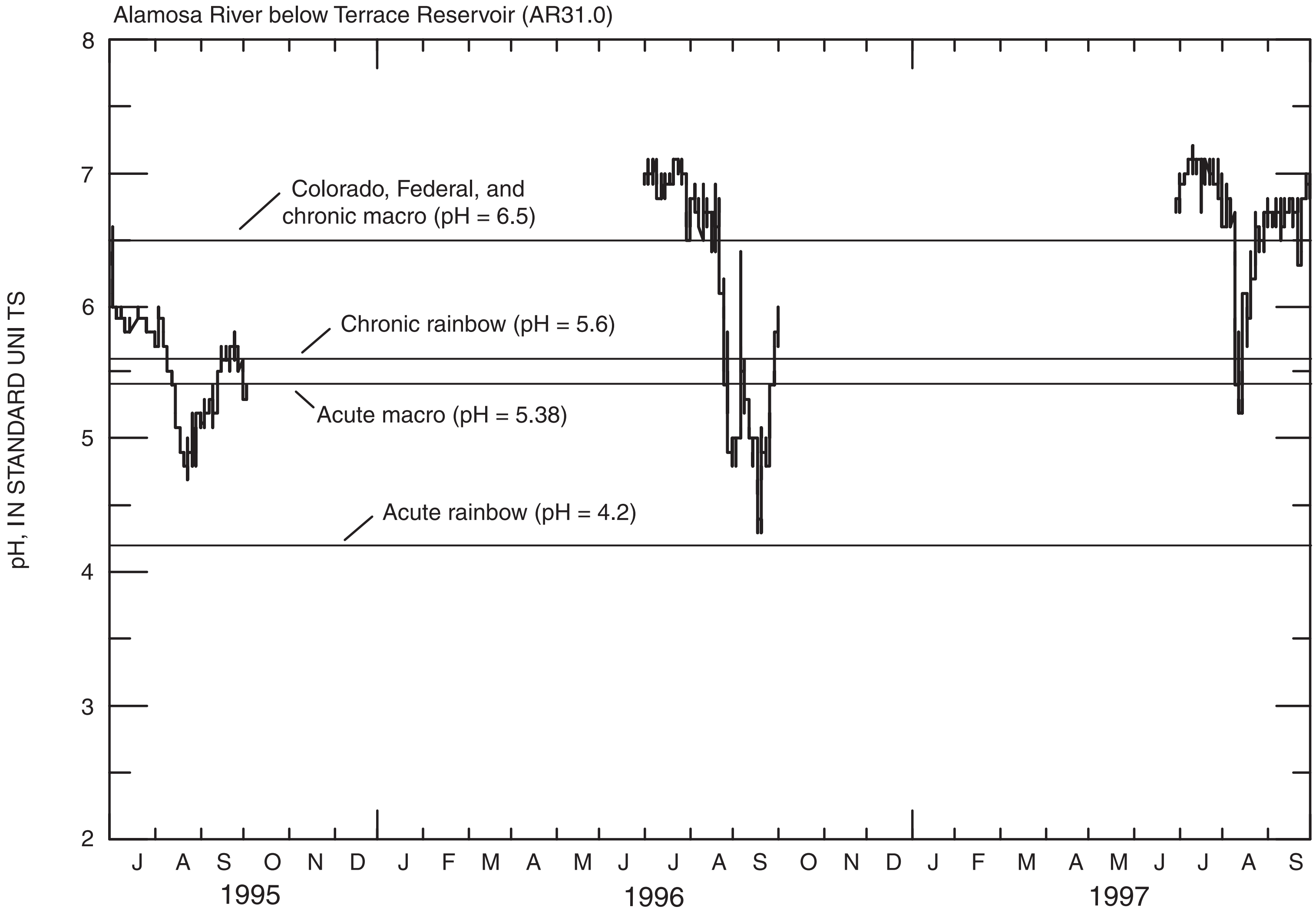

Figure 13. Colorado and Federal water-quality standards, Toxicological Reference Values, and pH at Alamosa River below Terrace Reservoir (AR31.0), upper Alamosa River Basin, July 1, 1995, through September 30, 1997. [TRV.xicological Reference Value; Colorado, Colorado water-quality standard, pH = 6.5; Federal, Federal water-quality standard, pH = 6.5; chronic macro, chronic TRV for benthic macroinvertebrates, pH = 6.5; Chronic rainbow chronic TRV for adult rainbow trout, pH = 5.6; Acute macro, acute TRV for benthic macroinvertebrates, pH = 5.38; Acute rainbow, acute TRV for adult rainbow trout, pH = 4.2]

water-quality standard for pH in the river segments near AR41.2 (EA-3b), AR34.5 (EA-3c), and AR31.0 (EA-5) is 6.5. The standard was seldom met at AR41.2 throughout most of the record and often was not met at AR34.5 and AR31.0 (figs. 11–13, table 7).

Toxicological Reference Values (TRVs) have been established for water quality in the upper Alamosa River Basin (Camp Dresser and McKee Corporation, 1999). TRVs define the level below which a constituent or property of water may produce an adverse physiological effect to a particular aquatic species. The chronic TRV for benthic macroinvertebrates (pH = 6.5) was rarely met at WF5.5 and WF0.0 (figs. 8–9, table 7). The acute TRV for benthic macroinvertebrates (pH = 5.38) and the chronic TRV for adult rainbow trout (pH 5.6) were rarely met at the Wightman Fork sites (WF5.5 and WF0.0) but were met more often at the Alamosa River Sites (AR45.5, AR41.2, AR34.5, and AR3l.0 (figs. 10–l3, table 7). The acute TRV for adult rainbow trout (pH = 4.2) was usually met at the Alamosa River sites but was rarely met at WF5.5. At WF0.0, the acute TRV for adult rainbow trout was met only about one-half the time in 1995 but was usually met in 1996 and 1997.

Aquatic organisms are sensitive to the duration of their exposure to decreased pH values. Most rainstorm runoff events resulted in decreased pH values for more than 4 hours (table 5). However, the individual rainstorm runoff events never resulted in decreased pH values for more than 96 hours, which is the largest time period typically used to determine acute exposure.

Relation Between pH and Metal Concentrations

Relations between pH and streamflow, specific conductance, dissolved aluminum, dissolved copper, dissolved iron, and dissolved zinc concentrations were evaluated for all sites during 1994–97. In general, an inverse log-log relation exists between pH and the logarithm of dissolved metal concentrations (figs. 14–18), indicating that as pH decreases, metal concentrations generally increase. To quantify the extent to which each relation approximates a log-log relation and the amount of variation in metal concentrations that can be explained by pH, the coefficient of determination (r^2) was calculated (Ott, 1993). A weak relation exists if r^2 is near zero, and a strong relation exists as r^2 approaches one. Most r^2 values are less than 0.8. Spearman's rho rank-order correlation coefficient (SR) (Ott, 1993, p. 465) was also calculated for each relation. The SR measures the monotonic association between pH and streamflow, specific conductance, or dissolved metal concentrations, even if the relation is not linear. A weak relation exists if SR is near zero and a strong relation exists as SR approaches one; a plus or minus sign indicates the slope of the relation. In many cases, SR values were larger than r^2 values but were still less than ±0.8 (figs. 14–18). Although a general relation exists between pH and dissolved-metal concentrations, figures 14–18 show that a large range in metal concentrations were observed for the same pH value. For instance, when pH at AR41.2 was about 5, dissolved aluminum concentrations ranged from about 500 µg/L to about 4,000 µg/L (fig. 17). These relations generally are not significant enough to confidently predict metal concentrations on the basis of measured pH values.

Wightman Fork below Cropsy Creek (WF5.5)

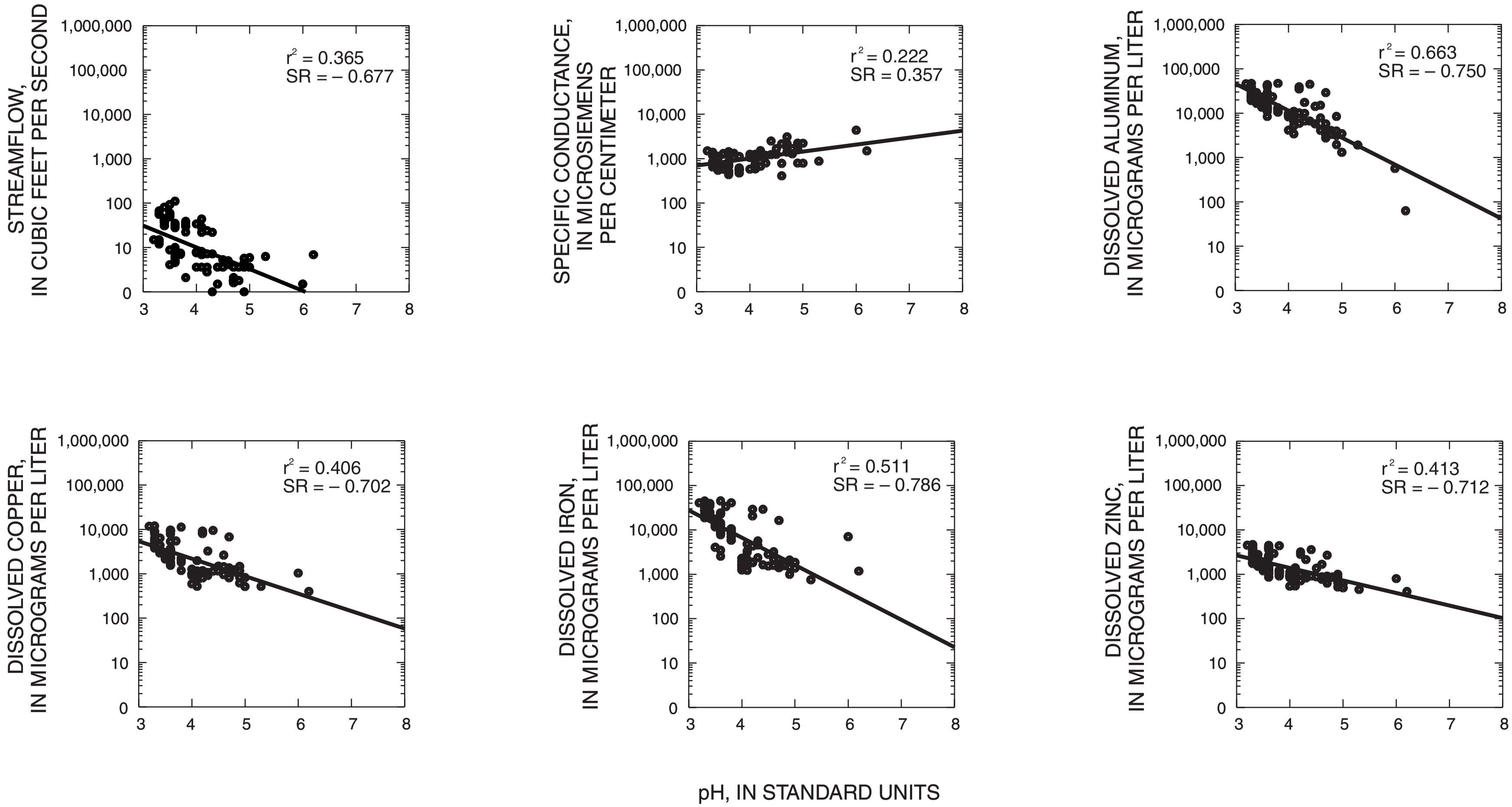

Figure 14. Relations between pH and streamflow, specific conductance, and selected metal concentrations, 1994–97, at Wightman Fork below Cropsy Creek (WF5.5), upper Alamosa River Basin, southwest Colorado. [r^2, coefficient of determination; SR, Spearman's rho]

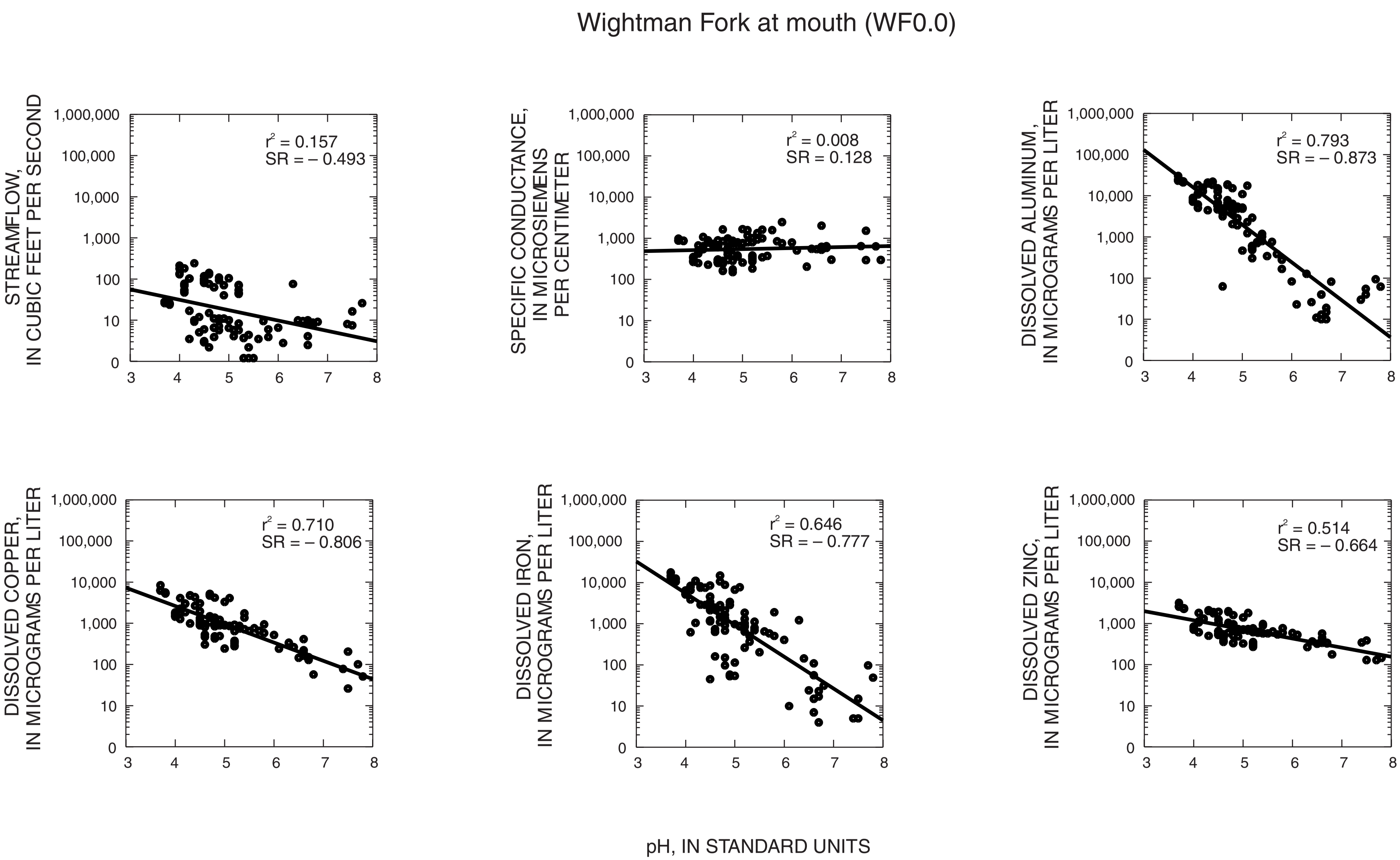

Figure 15. Relations between pH and streamflow, specific conductance, and selected metal concentrations, 1994–97, at Wightman Fork at mouth (WF0.0), upper Alamosa River Basin, southwest Colorado. [r^2, coefficient of determination; SR, Spearman's rho]

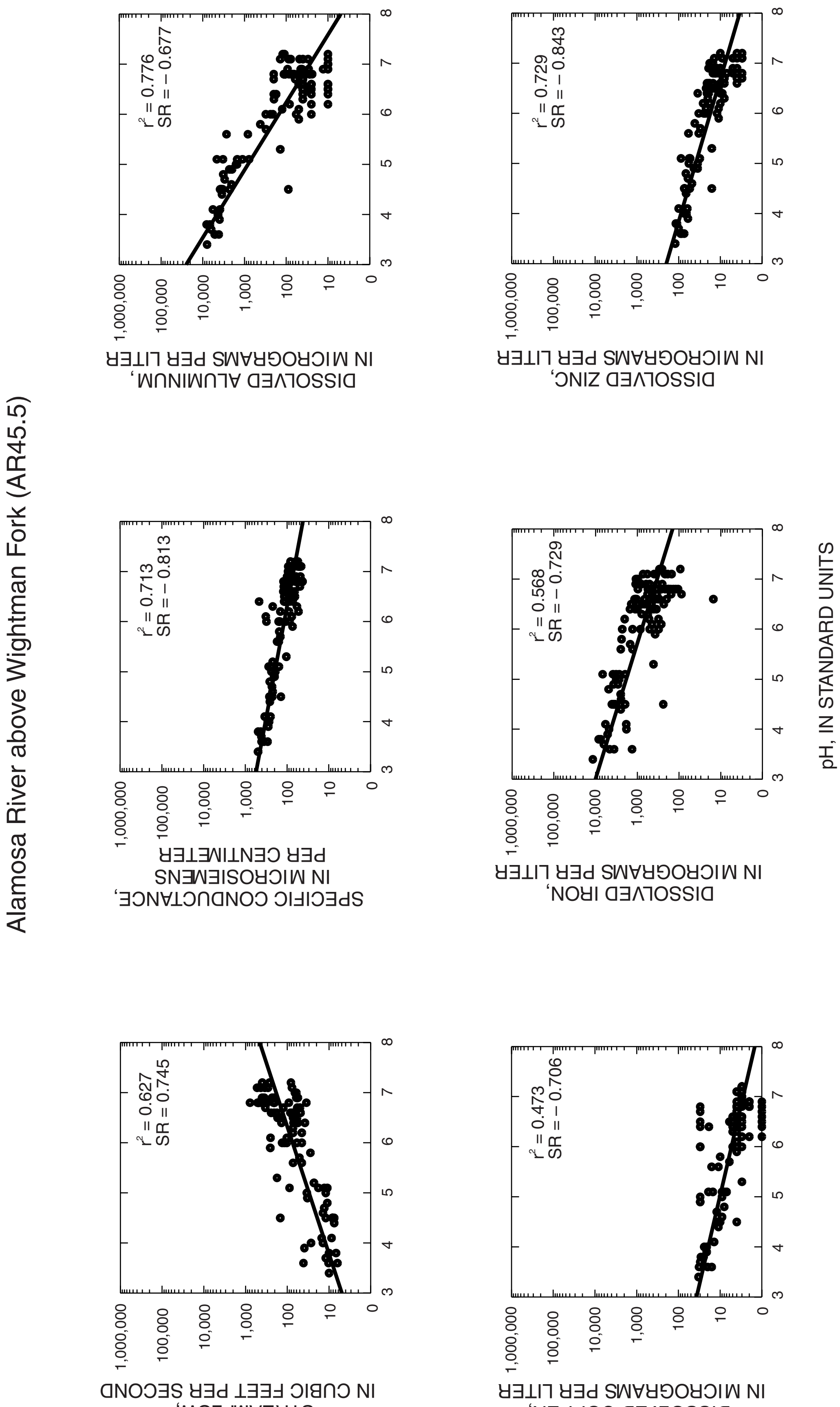

Figure 16. Relations between pH and streamflow, specific conductance, and selected metal concentrations, 1994–97, at Alamosa River above Wightman Fork (AR45.5), upper Alamosa River Basin, southwest Colorado. [r^2, coefficient of determination; SR, Spearman's rho]

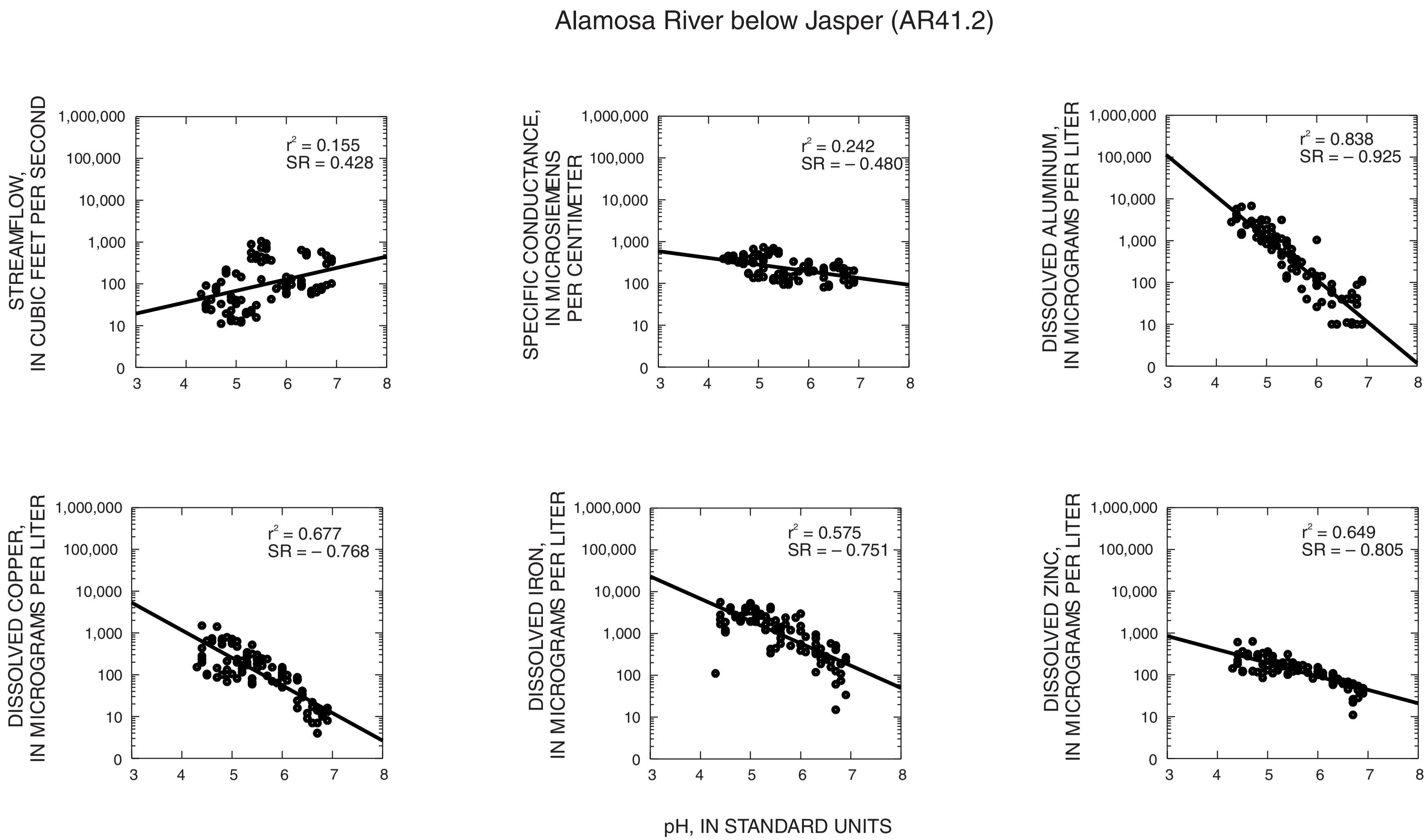

Figure 17. Relations between pH and streamflow, specific conductance, and selected metal concentrations, 1994–97, at Alamosa River below Jasper (AR41.2), upper Alamosa River Basin, southwest Colorado. [r^2, coefficient of determination; SR, Spearman's rho]

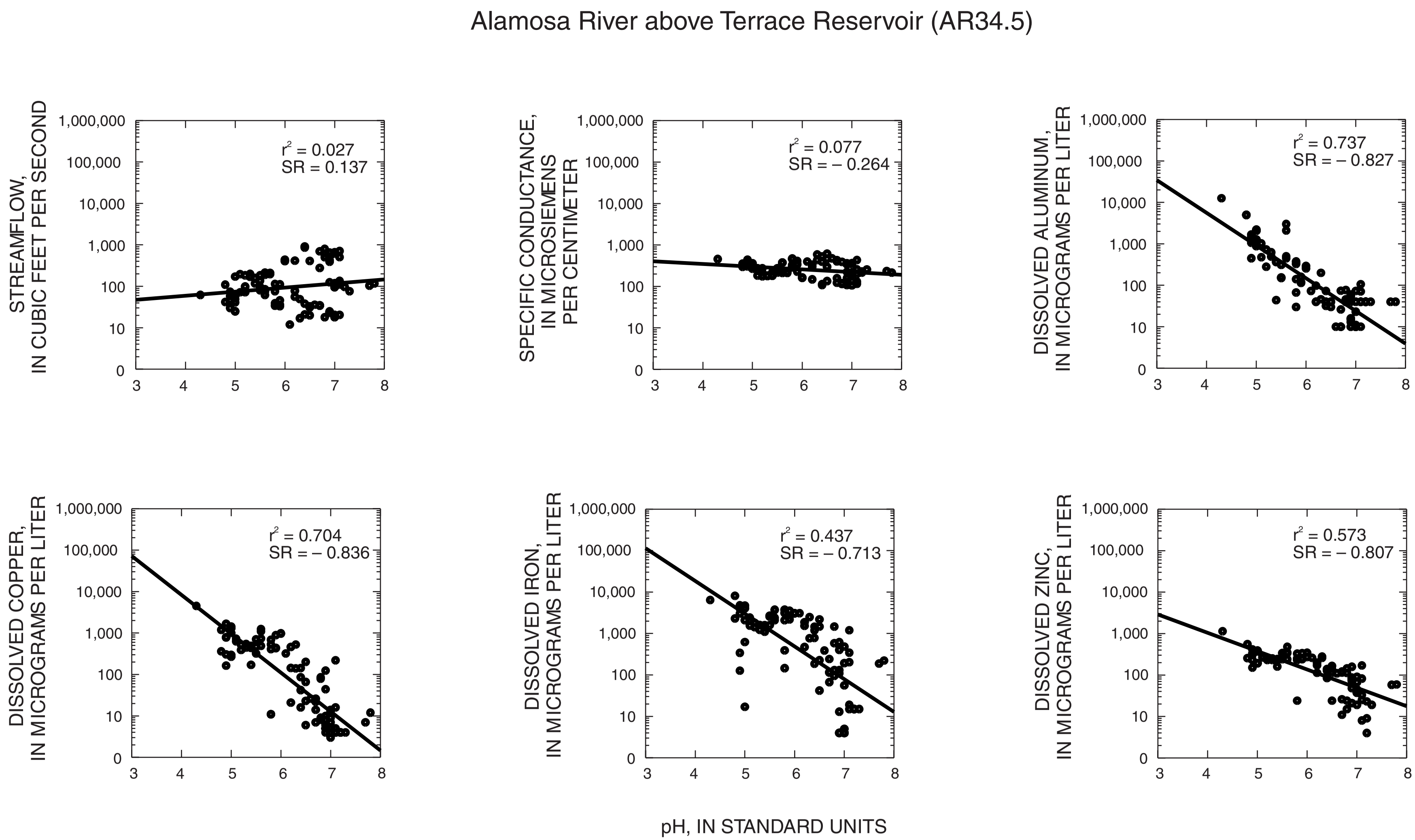

Figure 18. Relations between pH and streamflow, specific conductance, and selected metal concentrations, 1994–97, at Alamosa River above Terrace Reservoir (AR34.5), upper Alamosa River Basin, southwest Colorado. [r^2, coefficient of determination; SR, Spearman's rho]

SUMMARY AND CONCLUSIONS

Rainstorm runoff can have a significant effect on pH of waters in the upper Alamosa River Basin. Frequently, when rainstorms occur in the basin, streamflow rapidly increases and pH rapidly decreases. In some cases, pH decreased by more than 1 pH unit in response to rainstorm runoff. The sudden decreases in pH can have negative effects on aquatic life because the periods of low pH commonly last more than 4 hours.

The number of rainstorm runoff events that occurred between July 1 and September 30 was 17 in 1995, 18 in 1996, and 19 in 1997. Rainstorm runoff events were identified by observing streamflow records. Runoff events were identified when instantaneous streamflow increased at least 10 percent during a 1-hour period. Although the number of events was about the same each year of the study, the magnitudes and effects on pH differed. The changes in streamflow due to rainstorm runoff were significantly less at all sites in 1996 than in 1995 and 1997 because the study area had overall lower flows in 1996. The changes in pH due to rainstorm runoff were larger in 1996 than in 1995 and 1997 at most sites, possibly because of less water in the river and, thus, less water available for dilution.

Ninety-three percent of the rainstorms evaluated for this study produced runoff throughout the entire basin. During 1995–97, 54 storms occurred, but only 3 storms were isolated to the reach upstream from site AR45.5, and only 1 storm was isolated to the reach between sites AR4l.2 and AR34.5. Although most runoff events occurred throughout the entire basin, pH changes were most significant in parts of the basin that receive runoff from hydrothermally altered areas. The three principal altered areas within the basin are the Stunner, Summitville, and Jasper areas. Only limited mining occurred in the Stunner altered area, and yet significant decreases in pH values occur due to runoff from this area. Even after environmental restoration activities are completed at the Summitville Mine, the main stem of the Alamosa River may continue to be adversely affected by runoff from the Stunner and Jasper altered areas.

Discharge of untreated effluent from the Summitville Mine impoundment can significantly decrease pH values in the Alamosa River as far downstream as Terrace Reservoir. On July 10, 1997, untreated effluent was released from the impoundment to Wightman Fork. Although the streamflow in Wightman Fork was increased by only 3 ft^3/s, the pH in Wightman Fork decreased by about 1 pH unit. As the pH front moved down the river, pH decreased by about 1 unit at WF0.0, AR41.2, and AR34.5. The water stored in the impoundment apparently was highly concentrated because although streamflow increased by only 3 ft^3/s, the pH at AR34.5 decreased by 1 pH unit with a streamflow of more than 100 ft^3/s.

Rainstorm runoff from Terrace Reservoir may affect the pH of water in Terrace Reservoir and may pose a significant risk to aquatic organisms during low-flow years. During 1996, the basin had streamflows that were lower than during 1995 and 1997. Water storage and pool size of Terrace Reservoir also were lower than during 1995 and 1997. During August 21–29, 1996, the basin experienced a series of relatively low-intensity, long-duration rainstorms. On August 22, 1996, pH at AR34.5 decreased from approximately 6.3 to approximately 4.7. Approximately 38 hours later, pH at AR3l.0 decreased from about 6.7 to about 4.8. On September 2, the pH at AR34.5 increased to approximately 6.5, but the pH at AR31.0 remained less than 5.8 through the end of September. During September 12–25, the basin also had some small rainstorms, and streamflow at AR34.5 ranged from about 25 ft^3/s to more than 40 ft^3/s. During this time, the pH at AR34.5 was never less than 6.0, but pH at AR31.0 ranged from 4.3 to about 5.4. Geochemical interactions between sediment and the water column within the reservoir are a possible cause of the anomalously low pH.

A comparison of pH with Federal and State of Colorado water-quality standards and Toxicological Reference Values (TRVs) indicates pH did not meet the standards or TRVs in many parts of the basin. The USEPA has established a freshwater chronic exposure criterion for pH of 6.5 to 9.0 units. At all sites examined in this study, the pH was less than 6.5 for extended periods of time. The State of Colorado has established pH standards for most stream segments in the Alamosa River drainage. These water-quality standards for pH were not met at AR45.5 on numerous occasions and were rarely met during most of August 1996. The standard was seldom met at AR41.2 throughout most of the record and was rarely met at AR34.5 and AR31.0. Toxicological Reference Values (TRVs) are pH values below which adverse physiological effects may occur to a particular aquatic species. The chronic TRV for benthic macroinvertebrates (pH = 6.5) was rarely met at WF5.5 and WF0.0. The acute TRV for benthic macroinvertebrates (pH = 5.38) and the chronic TRV for adult rainbow trout (pH = 5.6) were rarely met on the Wightman Fork (WF5.5 and WF0.0) but were met more often at the Alamosa River sites (AR45.5, AR41.2, AR34.5, and AR31.0). The acute TRV for adult rainbow trout (pH = 4.2) was usually met at the Alamosa River sites but was rarely met at the Wightman Fork sites.

Relations between pH and streamflow, specific conductance, dissolved aluminum, dissolved copper, dissolved iron, and dissolved zinc concentrations were evaluated for all sites during 1994–97. In general, an inverse log-log relation exists between pH and the logarithm of dissolved-metal concentrations, but the relations generally are not significant enough to confidently predict metal concentrations on the basis of measured pH values.

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